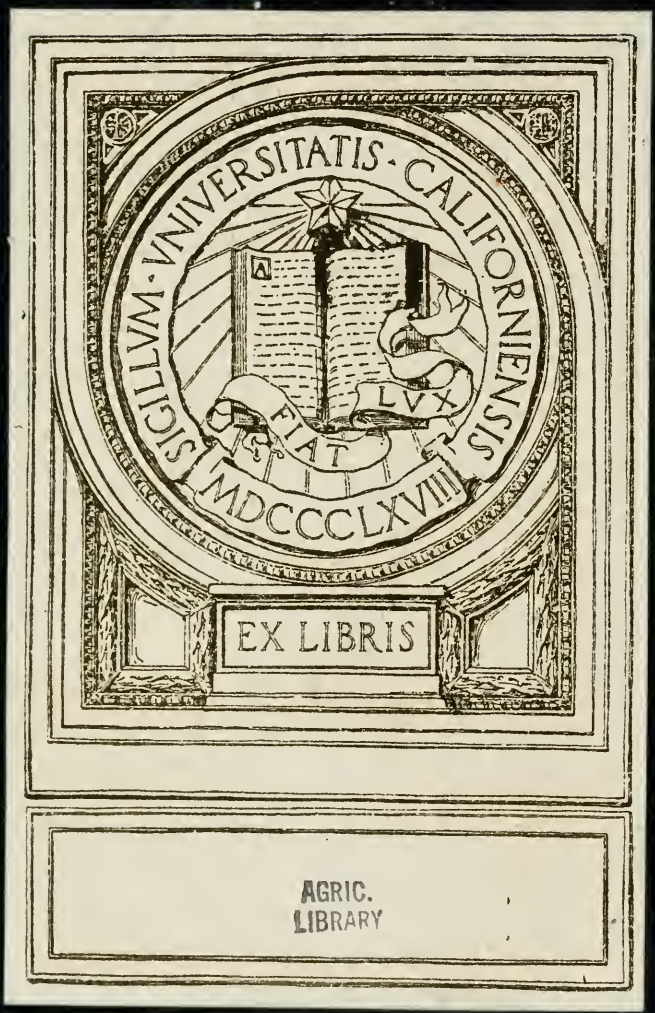
THE MANUFACTURE OF CHEMICAL MANURES

J. FRITSCH



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MANUFACTURE OF CHEMICAL MANURES

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THE MANUFACTURE OF CHEMICAL MANURES

BY

J. FRITSCH

TRANSLATED FROM THE FRENCH, WITH NUMEROUS NOTES, BY

DONALD GRANT

WITH SIXTY-NINE ILLUSTRATIONS AND ONE HUNDRED AND EIGHT TABLES

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AUTHOR'S PREFACE.

NOTWITHSTANDING the magnitude which the manufacture of Chemical Manures has assumed in France, no author has hitherto attempted to make it the subject of a special treatise in the French language. The author has endeavoured to fill this gap in spite of the difficulties inherent to the subject.

From a technical point of view, French literature supplies but little material for such a purpose. French chemists and works managers rarely write. They are tied down by professional secrecy, and when they do risk writing their prose is complicated by an embarrassed reticence which deprives it of all practical interest. Foreign publications, German especially, are better equipped in this respect. In addition to numerous special treatises, annual reports on the progress of different industries are available, edited most often by retired practical men or by old works managers, knowing everything, calling things by their names, discussing the value of the new processes recommended or applied, pointing out their merits and defects.

The numerous and valuable data which the author has thus collected have largely recompensed him for the ill-will which he encountered elsewhere. Certain constructors, it is true that they are not precisely at the head of mechanical progress, made a wry face. Others omitted to reply to our letters. This explains why French engineering firms are but little represented in this treatise. This explanation is due to the reader : it is for him to draw the moral.

The author, however, hastens to add that he met with the best reception from specialists eminent by their knowledge and long experience, and obtained from them the most complete information. He here returns them his sincere thanks, as well as to the scientists who have aided him by their counsel and encouragement.

The author makes no pretension of presenting a perfect treatise, yet he is confident that it will be useful to every one in any way connected with chemical manures.

PARIS, *March*, 1909.

25660 I

TRANSLATOR'S PREFACE.

From a long experience as works manager and chemist in the sulphuric acid and chemical manure trade, the translator has been able to add from his own knowledge acquired in actual practice numerous original practical notes to the English edition of M. Fritsch's work, solely with the object of increasing the utility of the treatise. It is to be hoped that the book which, independent of these notes, has unique merits of its own, will appeal in its English dress not only to manure manufacturers but to farmers themselves, as well as to agricultural students and all those who take an intelligent interest in the subject of agricultural chemistry. Common sense dictates that it is equally important for the student of agriculture to be able if need be to effect the synthesis of a manure as to be able to carry out the analysis thereof. The student who can construct mentally a formula for a manure to yield, whether by dry mixing or wet mixing, certain predetermined results on analysis, is more highly trained than he who can only use the faculties of destruction to resolve a manure into its constituent elements by slavishly following a treatise on agricultural chemical analysis, and that too often by methods which he would have to unlearn if he entered a manure factory, where he would have to analyse manures and raw materials against chemists of world-wide reputation.

DONALD GRANT.

May, 1911.

CONTENTS.

CHAPTER I.

PHOSPHORIC ACID.

PAGES

History—Origin and distribution of phosphoric acid in nature—Properties of phosphorus—1. Physical properties—2. Chemical properties—Hypophosphorous acid—Phosphorous acid—Phosphoric acid—Metaphosphoric acid—Pyrophosphoric acid—Orthophosphoric acid—Monometallic orthophosphate—Dimetallic orthophosphate—Trimetallic orthophosphate—Phosphate of lime—Monocalcic phosphate or acid phosphate of lime $CaH_4(PO_4)_2$—Dicalcic phosphate or monacid phosphate of lime—Tricalcic phosphate—Neutral phosphate of lime—Tribasic phosphate of lime $Ca_3(PO_4)_2$—Phosphates of ammonium and sodium—Basic phosphate of ammonium $(NH_4)_3PO_4$—Monacid phosphate of sodium (ordinary commercial phosphate of soda $Na_2HPO_4+12H_2O$)—Monacid phosphate of ammonium and sodium—Monacid phosphate of ammonium—Monacid phosphate of magnesium—Double phosphate of ammonium and magnesium $NH_4MgPO_4+6H_2O$—Phosphates of iron—The phosphates of alumina 1-13

CHAPTER II.

PRINCIPAL PHOSPHATE DEPOSITS.

I. France:—Pas de Calais, Somme, Oise—1. Somme phosphate—2. Pas de Calais phosphates—3. Meuse and Ardennes phosphates—4. Côte d'Or phosphates—5. Cher phosphate—6. Quercy phosphates (Lot and neighbouring departments)—7. Gard and Ardeche phosphates—8. Drôme and Isère phosphates—9. Pyrenees or Arièges phosphates. II. Belgium:—Ciply phosphates—Liége phosphates. III. England:—Lyme Regis coprolites—Cambridge coprolites—Suffolk coprolites. IV. Sweden and Norway:—Norwegian apatite. V. Germany. VI. Austria-Hungary:—Bohemian phosphates. VII. Russia. VIII. Spain:—Estremadura apatite. IX. North America:—Canada—South Carolina—Land phosphate and river phosphate—Florida—Hard rock—Plate rock or sheet rock—Soft phosphate—River pebbles—Land pebbles—Tennessee—Tennessee rock phosphate—Remarks on the actual condition of the phosphate industry in America. X. Africa:—Tunis and Algeria—Marly phosphates in nodules—Phosphatic limestones. XI. Asia:—Phosphates of Oceania. (I.) West India Islands:—Redonda Isles, Sombrero, Navassa, Aruba, Curaçao, Los Roques, Alta Vela, Rata. (II.) Islands of the Pacific Ocean:—Baker, Jarvis, Malden, Fanning, Starbuck, Howland, Phœnix, Sidney, Enderbury, Minerva, Aves, Lacépède, Flint, Browse (? Brown), Fluon, Chesterfield, Abrolhos, Mona, Cayman, Clipperton, Nauru, Angaur, Makatea, etc. (I.) West India Islands:—1. Redonda

PAGES

phosphate—2. Sombrero phosphate—3. Navassa phosphate—4. Aruba phosphate—5. Alta Vela phosphate—6. Rata or Fernando Noronjo phosphate—7. Monk's Island (Caribbean Sea) phospho guano—8. Christmas Island phospho guano. (II.) Pacific Ocean Isles:—Baker Island guano—Jarvis guano—Fanning Island guano —Brown Island guano—Mejillones guano—Lacépède Island guano— Clipperton Island guano—Angaur Island phosphate—Makatea Isle phosphatic deposits—Distribution of phosphates in the different geological formations. (I.) Gneiss Epoch. (II.) Paleozoic (or primary) epoch—1. Silurian formation—2. Devonian formation—3. Carboniferous formation. (III.) Mesozoic or secondary epoch—1. Trias formation—2. Jurassic formation—3. Cretaceous—Cainozoic or Tertiary epoch—Eocene formation—Quaternary and recent epoch - 14-49

Geographical distribution of phosphate of lime and guano deposits and their chemical composition—Table - - - - - - - - 50-59

CHAPTER III.

DRYING AND ENRICHMENT OF PHOSPHATES.

Drying—Calcining the nodules—Two tests—Different methods of strengthening and utilizing poor quality phosphates:—1. Dumonceau and Nicolas—2. Simpson—3. Brochon—4. Winsinger—5. O. Iahne —6. Martin—7. Thonnar and Huxton—8. Schucht—9. Carr—10. Glaser—11. Petermann—12. Hodgkins—Manufacture of precipitated phosphate by electrolysis - - - - - - - - - - 60-66

CHAPTER IV.

HISTORICAL REVIEW OF SUPERPHOSPHATE MANUFACTURE.

The manufacture of superphosphates from 1850 to 1870—1871 to 1880—1880 to 1894—1895 to 1908 - - - - - - - - 67-72

CHAPTER V.

THEORY OF MANUFACTURE OF SOLUBLE PHOSPHATES.

Effect of the impurities in phosphates on their behaviour in the process by which they are rendered soluble—Carbonates of lime and magnesia —Iodine—Calcium fluoride—Organic matter—Method of determining the amount of acid to use in order to render the phosphate soluble - - - - - - - - - - - - - 73-83

CHAPTER VI.

MANUFACTURE OF SUPERPHOSPHATE.

1. The grinding of the raw phosphate—2. Dissolving the ground phosphate in sulphuric acid—3. Drying the superphosphate—1. Grind-

PAGES

ing the raw phosphate—Crushers—Edge runners—Flatstone mills—Ball mill—Pfeiffer's mill, with combined air separator—Jaw-breaker mills—Cracking mills—Toothed roller mills—Disintegrators—Mills with percussion blades fitted in circular revolving boss—Elevators—Sieves—Filter press—Mixing of the phosphate with sulphuric acid—Evacuation of the toxic fumes - - - - - - - 84-110

CHAPTER VII.

CRUSHING, SIFTING, DRYING, AND STORING OF SUPERPHOSPHATE. RETROGRADATION.

Emptying and shifting the superphosphate house or den—New methods for the mechanical extraction of superphosphate from the "den"—Allegri's plant for shifting superphosphate from the "dens"—Breaking up and sifting or screening of superphosphate—Carr's disintegrator—Cylindrical crusher fitted with teeth—Cylindrical crusher, with two rolls fitted with teeth—Artificial drying of superphosphate—Theoretical review of drying—Möller and Pfeiffer's drying machine—Heymann and Nitsch's process for drying superphosphates—Dr. Lorenz' process—Dr. Lutjens' successor—Superheated superphosphates—Drying superphosphates in the cold—Drying of the superphosphate by dusting and mixing in the Georges crusher-sifter—Storing (preservation) of superphosphate—Retrogradation (reaction) of phosphoric acid—Forestalling retrogradation by Schucht's method - - - - - - - - - - - - - 111-141

CHAPTER VIII.

COMPOUND MANURES.

Superphosphate of ammonia—Ammoniated superphosphate—Superphosphate of ammonia and potash—Nitrophosphate—Tables for the calculation of "superphosphate of ammonia"—Dry mixings - 142-150

CHAPTER IX.

THE MANUFACTURE OF PHOSPHORIC ACID, DOUBLE SUPERPHOSPHATES AND VARIOUS PRODUCTS.

Historical review—Manufacture of phosphoric acid—Manufacture of double superphosphate—Manufacture of superphosphate of potassium and ammonium—Manufacture of sulpho-phosphates—Bisulphate superphosphate—Phosphatic peat - - - - - - 151-166

APPENDIX.

THE MANUFACTURE OF PHOSPHORUS IN THE ELECTRIC FURNACE.

Wing's process—Readman's patent—Harding's process—Gibb's furnace—Irvine's furnace—Duncan's patent—Parker's patent—Landis' method - - - - - - - - - - - - - 167-172

CHAPTER X.

PAGES

MANUFACTURE OF BONE DUST AND OF BONE SUPERPHOSPHATE (VITRIOLIZED BONES).

Fertilizing value of bone—Storing, classifying, sorting and crushing bones—Storing—Classification of bones—1. Kitchen bones—2. Horse bones or knackers' bones—3. Buried bones—4. Bullocks' heads (sheep's heads)—5. Scraps and waste—6. Hornpiths—Bone picking—Bone crushing—1. Slow-speed crusher—2. Very quick-speed machine—Extraction of fat from bones—1. Extraction of fat from bones by water—2. Fat extraction from bones by steam—3. Extraction of fat from bones by benzine—Purification of bone fat—Bleaching of brown bone fat—Manufacture of bone dust—Classification of bone dust—1. Normal bone dusts or bone dust No. 0—2. Bone dusts (without any other designation)—3. Degelatinized bone dusts—4. Mixed manure dusts—Meat dust (meat meal)—Adulteration—Manufacturing of bone superphosphates—Vitriolized bones—Vitriolated bones—Mixture of bone superphosphate (dissolved bones) and nitrogenous matter—Blood—Horn—Leather waste—Animal Charcoal—Bone ash—Manufacture of precipitated phosphate of lime - - - - - - - - - - - - - - 173-196

CHAPTER XI.

MANUFACTURE OF BASIC SLAG.

Origin of basic slag—The nature of basic slag—Tetraphosphate of calcium—Solubility of basic slag—Crushing of basic slag—Remarks on the use of basic slag—Graphic illustrations of the manufacture of basic slag—Basic slag contracts—Sampling analysis - - - - - 197-217

CHAPTER XII.

NITROGENOUS MANURES.

Nitrate of soda—Nitric acid—Chili nitrate of soda—The caliche terra salitrosa—1. Open cast-iron pans—Paradas—2. Cylindrical vertical pans—Maquinas—3. Vessels heated by a closed tubular bundle (?steam coil)—Storing and handling of nitrate—Production of nitrate in 1907—Ammoniacal salts—Manufacture of sulphate of ammonia by distillation of gas liquor—Production of ammonia in the manufacture of coke—Recovery of ammonia from blast furnaces—Recovery of ammonia formed in gas producers—Siemens', Schilling's, Powson's, Wilson's and Mond's—Mond's process—2. Bourgeois and Lencauchez's process—Manufacturing plant—Condensers—Standard washer—Distilling plant—Naked fire stills—The English still—Mallet's still—Lunge's still—Feldmann's still—Gruneberg and Blum's still—Manufacture of sulphate of ammonia from urine—Utilization of peat in the manufacture of ammoniacal salts—Recuperation of the ammonia—Gaillot and Brisset process—Muntz and Girard's process—Manufacture of sulphate of ammonia from peat by the Mond process—Crude ammonia from spent oxide - - 218-254

CHAPTER XIII.

PAGES

MANUFACTURE OF MANURE FROM ANIMAL WASTE.

Preliminary remarks—Blood—Dried blood—Donard and Boulet's drying machine—Meat meal—Drying blood by lime—Commercial meat meal—Horn—Leather waste—Comparative value of different nitrogenous manures - - - - - - - - - - - - 255-267

CHAPTER XIV.

RECOVERY OF NITROGEN FROM DISTILLERY SPENT WASH. MANUFACTURE OF CYANAMIDE AND OF NITRATE OF LIME.

Utilization of distillery spent wash—General remarks—Recovery of nitrogen by Vasseux's process—Treatment of the spent wash by biological agents—Effront's methods—Treating spent wash by fermentation—The manufacture of cyanamide and of nitrate of lime—Agricultural experiments with cyanamide—Rules for the use of cyanamide—Drawbacks in the use of nitrate of lime - - 268-277

CHAPTER XV.

NITROGENIZED PHOSPHATIC MANURES.

Peruvian guano—Its composition—Dissolved Peruvian guano—Other nitrogenized guanos—Bat guano—Hungarian bat guano—Eboli bat guano—Egyptian bat guano—Fish guano: historical review—The early manufacture of fish guano in Newfoundland and in Great Britain—Manufacture of fish guano in Norway—The fish guano industry in Britain - - - - - - - - - - 278-294

CHAPTER XVI.

POTASSIC MANURES.

Stassfurt salts—Crude potash salts—1. Carnallite—2. Sylvine or sylvinite—3. Kainit—4. Schoenite—5. Polyhalite—6. Krugite—Dissolving the crude salts—Clarification—Crystallization—Clarifying—Treatment of the mother liquor from the potassium chloride—Drying the chloride of potassium—Potassium sulphate—Double carbonate of potassium and magnesium—Double sulphate of potassium and magnesium—Other fertilizing salts—Commercial brands of potassium chloride (muriate of potash)—Manufacture of potash from felspar and other potassic minerals—Manufacture of potash from sunflower stalks in the Caucasus - - - - - - 295-315

CHAPTER XVII.

PAGES

TRANSFERENCE AND HANDLING OF RAW MATERIALS AND FINISHED PRODUCTS.

Electric transhipment of phosphate and superphosphate in a manure factory—General arrangement of electrical conveying machinery in Pommersdorf chemical factory—General arrangement of electrical conveying machinery in Emmerich chemical manure factory—Electrical transhipment plant, St. Gobain's chemical factory, Boucau—Electrical transhipment plant in a German factory—Cable transhipment system of Algerian phosphate factory - - - 316-332

INDEX - - - - - - - - - - - - - 333-339

LIST OF TABLES.

TABLE		PAGE
I.	Showing percentage of phosphoric acid in various rocks	2
II.	Analyses of three different types of Somme phosphates	15
III.	Analysis of average sample of a field of Orville phosphate dried in vacuo at 98° C., density at 16° C. 3·1307. (H. Lasne)	16
IV.	Beauval phosphate deposit. Analysis made by Nantier at the date of discovery	16
V.	Analyses of Pas de Calais phosphates	18
VI.	Analysis of Meuse phosphates	19
VII.	Analyses of various phosphates in the Meuse, Ardennes, etc., districts. (Delattre)	19
VIII.	Analysis of Ardennes nodules. (Maret and Delattre)	20
IX.	Analyses of Auxois phosphates. (Delattre)	21
X.	Analysis of Quercy phosphates	22
XI.	Analyses of Ciply phosphates	24
XII.	Analyses of Liége phosphates	24
XIII.	Analyses of Lyme Regis coprolites. (Thompson Herapath)	25
XIV.	Analysis of Cambridge coprolites	25
XV.	Analysis of Suffolk coprolites	25
XVI.	Analyses of fossil bones from Sutton bone bed	26
XVII.	Analyses of Suffolk, etc., coprolites	26
XVIII.	Analysis of Norwegian apatit (crystals)	27
XIX.	Analysis of Bohemian phosphates	27
XX.	Analysis of Russian phosphorite nodules	28
XXI.	Analysis of Central Russia phosphorite	28
XXIa.	Analyses of samples of Estremadura phosphates	29
XXII.	Average composition of Carolina phosphate	31
XXIII.	Analysis of a fine sample of hard rock phosphate	32
XXIV.	Analyses of hard rock phosphate from Blue River Co.	33
XXV.	Analysis of land pebble phosphate	35
XXVI.	Analysis of Tennessee rock phosphate	35
XXVII.	Complete analysis of an Algerian phosphate	38
XXVIII.	Analyses of two samples of Djebel Gournia phosphate in the natural condition	38
XXIX.	Analyses of Redonda phosphate	39
XXX.	Analysis of Sombrero phosphate. (Voelcker)	40
XXXa.	Analyses of Nevassa phosphate	40

TABLE		PAGE
XXXI.	Analysis of Alta Vela phosphate	41
XXXII.	Analysis of Monk's Island phosphate	41
XXXIII.	Analysis of Baker Island guano	43
XXXIV.	Analysis of Jarvis Island guano	44
XXXV.	Analyses of Fanning Island guano	44
XXXVI.	Analyses of Brown Island guano	44
XXXVII.	Analyses of Lacépède Island guano	45
XXXVIII. and XXXIX.	Analyses of Mejillones guano	46-7
XL.	Analysis of Clipperton Island guano	47
XLa.	Geographical distribution of phosphate of lime and guano deposits and their chemical composition	50-9
XLI.	Amount and strength of acid required to dissolve various phosphates	83
XLII.	Results of experiments with ordinary superphosphate and superphosphate dried at different temperatures on Ligouro oats	129
XLIII.	Showing changes in composition which Tennessee superphosphates undergo in four and a half months from date of making	137
XLIV.	Showing for a succession of years the increase in hay from one application of basic slag to a poor meadow	141
XLV.	Number of cwt. required in a 5 ton mixing, or of tons in a 100 ton mixing of a superphosphate of a given strength in P_2O_5 to produce a manure of a given strength in P_2O_5	146
XLVI.	Showing in cwt. the amount of sulphate of ammonia of different strengths that must be contained in a 5 ton heap to get a manure containing from 1·850 up to 5 per cent nitrogen	149-50
XLVII.	Showing the analysis of double superphosphate	156
XLVIII.	Chemical composition of ossein	173
XLIX.	Analysis of an ox bone. (Berzelius)	174
XLIXa.	Rosinate analysis of bones as supplied to manure factories	174
L.	Analysis of bone dust from fat extracted bones	185
LI.	Analyses of new and used and spent bone char. (Pierre)	192
LII.	Showing the composition of five samples bone ash. (Voelcker)	193
LIII.	Analysis of precipitated phosphate of lime	194
LIV.	Analysis of cast-iron showing phosphorus content	200
LV.	Analyses of crystals of tetrabasic phosphate of lime found in basic slag	204
LVI.	Analyses of hexagonal crystals found in basic slag	204
LVII.	Analyses of black needles, magnetic and non-magnetic, found in basic slag	206
LVIII.	Analyses of blue crystals found in basic slag	206
LIX.	Solubility of basic slag in water saturated with carbonic acid	209
LX.	Showing the results of Jensch's researches on basic slag	210
LXI.	Effect of composition of basic slag on facility of grinding	213
LXII.	Showing the influence of the ratio of the peroxide of iron to protoxide on the ease of grinding of basic slag	213

TABLE		PAGE
LXIII.	Analysis of blue and brown crystals in basic slag	216
LXIV.	Showing composition of caliche	220
LXV.	Analysis of Chilian nitrate of soda	221
LXVI.	Analysis of better quality nitrate of soda	221
LXVII.	Analyses of a double nitrate of potash and soda	222
LXVIII.	Analyses of gas liquor from coals of different origin	226
LXIX.	Analysis of British gas liquor	226
LXX.	Analysis of spent Lamming's mixture from gas works	251
LXXI.	Percentage of different nitrogen compounds present in a series of samples of spent oxide from gas works	252
LXXII.	Table for conversion of nitrogen per cent into ammonia per cent and vice versa	254
LXXIII.	Analyses of bullocks, calves, sheep, and pigs' blood	256
LXXIV.	Composition of meat meal	262
LXXV.	Showing agricultural value of nitrogenous manures (nitrate 100)	267
LXXVI.	Showing comparative agricultural money value of nitrogenous manure in francs per kilogram	267
LXXVII.	Showing value and amount of manure from spent wash from 1 ton molasses	270
LXXVIII.	Analyses of cyanamide	273
LXXIX.	Analyses of Peruvian guano	280
LXXX.	Analyses of Peruvian guano	280
LXXXI.	Analyses of Peruvian guano	281
LXXXII.	Analyses of Peruvian guano	281
LXXXIII.	Analyses of guano from middle bed of Peruvian guano deposits	283
LXXXIV.	Analysis of Peruvian guano nodules (lower bed)	283
LXXXV.	Analyses of different cargoes of Peruvian guano	284
LXXXVI.	Analysis of bat guano	287
LXXXVII.	Analysis of Hungarian bat guano	287
LXXXVIII.	Analysis of Egyptian bat guano	288
LXXXIX.	Analysis of Eboli bat guano	288
XC.	Analysis of Brittany fish guano	291
XCI.	Analyses of Norwegian fish guano	293
XCII.	Showing the composition of nitrogenous manures	294
XCIII.	Potash content of various plants	295
XCIV.	Analysis of first borehole sample of Stassfurt potash salts	297
XCV.	Analysis of carnallite	298
XCVI.	Analysis of sylvinite (pure)	298
XCVII.	Analysis of sylvine as it comes from the mine	299
XCVIII.	Showing analysis of kainit. (Reichardt)	299
XCIX.	Analysis of polyhalite	300
C.	Analysis of krugite. (Mercker)	301
CI.	Analysis of crystals from potash salt crystallizers	303
CII.	Analysis of mother liquor from clarification of potash salts	304
CIII.	Analysis of mother liquor from potassium chloride	305

TABLE		PAGE
CIV.	Analysis of schoenite. (Mercker)	307
CV.	Analysis of sludge from clarification of potash salts	308
CVI.	Composition of Stassfurt potash salts	309
CVII.	Chlorine content of crude potash salts	311
CVIII.	Effect of soluble mineral salts on grain crops	313

CHAPTER I.

PHOSPHORIC ACID.

History.—The discovery of phosphorus is due to the alchemists. In 1669, Brandt, a Hamburg merchant, searching for the philosopher's stone in human urine, discovered an interesting substance which he called *phosphorus*, i.e. a body luminous in the dark. All the phosphori known up to then—and there was quite a series of them—to become luminous had to be previously exposed to sunlight, and yet their luminosity soon vanished, whilst the new body emitted a glow of its own accord, and preserved that property permanently. It was, therefore, termed *phosphorus*. Brandt kept his process secret. But, in his turn, Kunkel, a Berlin chemist, soon discovered phosphorus. In 1688, Albinus extracted phosphorus from mustard seed and cress seed. Thus within a few years phosphorus was found in both the animal and vegetable kingdoms without, however, anyone dreaming of its connexion with inorganic nature. According to the cosmic theories of the times this substance was held to be the product of other bodies, or even the result of spontaneous generation under the influence of ill-defined vital forces. The scientists of the time had not yet distinguished the chemical elements, the very simple theory of which was destined in the future to furnish the very basis of the science of these bodies.

It is interesting, however, to observe that free phosphorus was prepared and examined for seventy years without its compound with oxygen, phosphoric acid, from which it had been isolated and to which it so easily reverts, being known. Phosphoric acid was not discovered till 1743, by Margraff, who ascertained its exact nature and succeeded in re-converting it into phosphorus by calcining it with charcoal. In 1769, Gahn, a Swedish chemist, found this acid in bones, and a few years later Scheele, his countryman, published a process by which phosphorus could be extracted from bones, which is still used in its main features.[1] Ten years after the discovery of phosphoric acid in bones, and more than 100 years after the first preparation of phosphorus, Gahn found this body in the mineral kingdom also, viz. in lead phosphate (pyromorphite): Vauquelin and Klaproth soon afterwards found phosphoric acid in apatite, that beautiful mineral, met with in large masses, the com-

[1] Scheele was by birth a Prussian. See Scheele's "Chemical Essays," Scott, Greenwood and Son.

position of which is analogous with the earthy parts of bone. Such are, briefly summarized, the chief historical facts regarding the discovery of phosphorus and phosphoric acid in the three kingdoms of nature. Since then chemists have continued their investigations; they have searched for this substance everywhere, and they have found it more and more as analytical methods have been improved. Its presence in urine and in bones led to its presence in all the fluids and organs of man and animals being suspected, and very soon it was found to be so. It was found in all plants and in all their organs. It was thenceforth recognized that the phosphorus contained in the body of animals was of vegetable origin. But from whence do plants derive this substance? The answer to that question was sought for a long time. Even up to the middle of the eighteenth century, when scientists like Saussure (1740-1799) and others were led by simple logic to look for phosphoric acid in the soil, agronomists persisted in regarding it as a derivative of other substances, because very little of it was found in the soil, and this little might very well be brought on to the land by farmyard dung. However, improved analytical methods were bound gradually to elicit the truth.

Origin and Distribution of Phosphoric Acid in Nature.—If it be interesting for the farmer and the chemist to follow the migrations of an air-bell, and the curious phenomena under the influence of which the molecule of nitrogen becomes successively ammonia or nitric acid, then vegetable organism, then finally muscular fibre, it is none the less instructive to follow the migrations of the molecule of phosphorus. Let us endeavour to grasp these migrations, and to trace them, starting from the point of origin of phosphoric acid, i.e. the presence of this body in the primitive and crystalline rocks. The analysis of the primitive rocks, and of the metalliferous veins which they contain, proves that phosphoric acid is almost always one of their constituent elements.[1] Associated with lime, the

[1] The two men of science who studied the question most profoundly were Forchammer of Copenhagen and Stockhardt of Germany. The latter found phosphoric acid in several rocks in which it was believed to be absent. The percentages of phosphoric found in different rocks are as follows:—

TABLE I.—PERCENTAGE OF PHOSPHORIC ACID IN VARIOUS ROCKS.

Rock.	Per cent.	Rock.	Per cent.
Feldspar (Rochsbourg) .	1·70	Melaphyre (Plauen) . .	0·38
Gneiss (Gerlusdorf) . .	0·78	Syenit (Plauen) . . .	0·18
Granulet (Penig) . .	0·63	Gneiss (Tharandt) . .	0·25
Granit (Hellsdorf) . .	0·58	Felsite (Tharandt) . .	0·21
,, (Burgstaldt) . .	0·68	Limestone (Schweindorf) .	0·51
Basalt (Tharandt) . .	1·10		

oxides of iron, manganese, lead and copper, this body constantly reveals its presence to the expert chemist who makes a special search for it. Its proportions are most often very minute, but that matters little, as plants have a marvellous faculty of freeing from the soil the principles necessary to their development. And let us remark with Bobierre, "how everything hangs on a chain, to explain to us the distribution of phosphoric acid in our crops. Let us go back, in imagination, to the origin of things, to those great natural phenomena, all the traditions in regard to which are in accordance with what geology reveals to us of these gigantic phases. The igneous rocks contain phosphoric acid. The disintegration of these rocks under the combined influence of water, air, temperature, and carbonic acid, soon favours the physical divisions of the rock masses. Vegetation develops, vivacious, luxuriant, immense, accumulating at the same time both carbon from the atmosphere—which it is to return as coal to far-off generations—and phosphates which its organs, immersed in a virgin soil, assimilate to abandon one day in a fine state of division on the surface of the soil. And as an energetic, active, incessant medium of this providential distribution, the animal world supervened with its powerful capacity of condensation of principles, rich in phosphorus and in nitrogen. Thus it is that vegetation supplies phosphates clothed in a new dress for the alimentary needs of new individuals. The molecule of phosphoric acid is no longer the inert crystalline portion of the igneous rock, it is no longer the mineral framework of the plant, it is the osseous substance of the animal, it is both its skeleton and its flesh, its nervous fibre, and its entire being. Our ideas of the organism and of phosphorus are inseparable the one from the other." The beds of the different geological periods all contain fossils, more or less rich in phosphoric acid. The Cambrian yields *Ligulides* and *Discenides*, forerunners of the *Brachiopods*, whose calcareous shells were comparatively rich in phosphoric acid. At a later period vertebræ appear; first, the Silurian fish, then the saurians of the Carboniferous and Permian, and finally, the birds (Jurassic) and mammals (Trias), the skeletons of which form the principal elements of the accumulation of phosphoric acid. Thus the soil of all formations may contain phosphates, but they are not found in large quantity except in certain formations and under peculiarly favourable circumstances, which we vaguely perceive, but of which it is impossible to give a really satisfactory explanation. The solution of phosphoric acid by rain water, charged with carbonic acid, traversing the superficial layer of soil covered with vegetation and thus rich in humus, its entrainment into the subsoil, and its accumulation in the subjacent rock, the chemical affinity of which favours its combination—such seems to be the genesis of phosphate deposits. Meeting lime, oxides of iron, and alumina the phosphoric acid solu-

tions form phosphates of lime, iron, and alumina. On the phosphate beds so formed new layers of phosphates were deposited as soon as the carbonic acid acting as the phosphoric acid solvent had set free sedimentary phosphates. When the solution percolated into hollows it formed pockets. The carbonated water could even convert already formed phosphate into a special form, for example that of vitreous staffelite. Nodules were formed when the rock to which the phosphoric acid was combined was deficient in consistency, or had lost it, for example owing to the upheaval of the deposit, the different portions of which were washed and removed by water, thus rounding the fragments. Nodules may again be formed by the fixation of phosphoric acid round a centre, for example around grains of sand swimming in the solution on the impulse of a crystal growing in an appropriate solution, or organisms or even bells of gas rising in the solution drawing to it particles of the same nature as itself. Finally, another hypothesis of the formation of nodules is that where precipitated phosphate of lime had been gradually reunited into compact nuclei by water through the intervention of pebbles of silex. Apatite was the first phosphate formed by the crystallization of the incandescent rocky magma. Its crystalline form is hexagonal. As it cooled slowly, the mass of liquid apatite formed crystals of different sizes, from capillary needles, scarcely visible, up to 12 in. in length. Their interior always assumes a lamellar structure. Apatite is found massive, with this crystalline structure, or even compact and massive when it is embedded in basalts. But compact massive apatite always comes from crystalline apatite. Pseudo-apatite is disintegrated apatite. All these forms of phosphate, from the crystalline form to the amorphous, from isolated nodules to rock phosphate, go back to an identical origin. Summing up, phosphorus existed in the beginning of things in the primitive rocks. It has become more assimilable in virtue of its distribution in sedimentary and transported soils; vegetables have absorbed it, then they have given it up to the animals, which have condensed and accumulated it in numerous points of the globe. Let us note, with Buckland, that it is astonishing that the human race should, for so many centuries, have remained ignorant of the fact that a considerable portion of the surface of the globe was formed by the debris of the animals which inhabited the ancient seas. There exists, according to the same author, vast plains and enormous mountains which are merely, so to speak, the charnel houses of preceding generations, in which the petrified debris of extinct animals and vegetables are piled up to form marvellous monuments. These monuments attest the work of life and death during incalculable periods. Cuvier, appreciating these curious natural phenomena, declared that the sight of such a spectacle as that of the debris of life forming almost all the soil on which our feet tread was so

terrible as to render it difficult for him to retain his imagination on the causes which have produced such great effects. These effects, so terrifying to the genius of Cuvier, are really only the result of one and the same cause—an efficient cause, which is confirmed under the most diverse conditions, and in all latitudes, with a wonderful unity of design. Only the Sovereign Master of Life and Death could accomplish such wonders. Let us now try to find the amount of phosphoric acid in different media—phosphoric acid in the soil, in plants and animals. About the time when British agronomists[1] were exploring the deposits of phosphate of lime of Estramadura, it was discovered, in Surrey, that the use of ground bones, and other bodies rich in phosphoric acid, produced no beneficial result when applied to soils, fertile enough in themselves, the subsoil of which belonged to certain deposits of the lower and upper Greensand. This led to the supposition that phosphate of lime, which is one of the fertilizing constituents of ground bones, is naturally present in these soils in sufficient proportion. Mr. J. C. Nesbit, an expert chemist, immediately collected the soils and rocks of these districts so as to ascertain the cause of their fertility. Amongst others, he received from Farnham samples of a fertile marl, situated on the property of Mr. J. M. Paine. A rapid examination showed the presence, in this marl, of an unusual amount of phosphoric acid, and in November, 1847, he informed Mr. Paine of this discovery.[2] From this marl 28 per cent of phosphoric acid, corresponding to 60·67 of phosphate of lime, was extracted. The general mass of the marl contained 2 to 3 per cent of phosphoric acid, equal to 4·33 to 6·5 per cent of phosphate. It will be seen that in presence of such a proportion of phosphoric acid the application of phosphatic manures was quite superfluous. In the *Tchermo Sem*, so fertile in Russia, where from time immemorial the highest yields of wheat have been obtained without any manure, 0·6 per cent of phosphoric acid is present, whilst mediocre soils only contain 0·1; fertile soils, 0·2 to 0·5; very fertile soils, 0·8 and upwards. Regarded by themselves these figures are very small, but applied to a given surface, are considerable. A hectare of arable land, say 2·5 acres, with a depth of 0·2 metre, say 10 in., weighs 5000 tons, say 2000 tons per acre, and if such soil contains 0·6 per cent of phosphoric acid that

[1] This very evidently refers to Dr. Daubeny, who inspected and reported on these deposits (Estramadura) in 1843. His report is given in the "Journal of the Royal Agricultural Society of England," Vol. V, Part II.—Tr.

[2] But Mr. Paine himself, in conjunction with Professor Way, the then chemist of the Royal Agricultural Society of England, in 1848 published the results of their then combined elaborate researches on the phosphoric strata of the chalk formation in a paper in the "Journal of the Royal Agricultural Society of England," Vol. IX, Part I, pp. 56-84. The reader is referred to this memoir: suffice it to mention here that the marl contains nodules much richer in phosphate of lime than the marl in which they are diffused.—Tr.

makes 30 tons of that acid per hectare or 12 tons per acre. The diffusion of phosphoric acid in arable land responds, moreover, to a providential law, that element being as indispensable to plant life as to animal life. In the absence of phosphoric acid, none of our cultivated plants can pass through all the phases of vegetation; the seed may germinate, produce leaves, stem, branches, but these organs remain attenuated, lingering, till the plant dies prematurely without bearing flowers or fruit. Corenwinder made researches to follow up phosphorus in plants. Analyses of roots, stem, and fruit proved that phosphorus exists in nascent organs where it contributes to organization. It diminishes proportionally in the root; thus the root of beet-root does not contain phosphorus after the maturity of the seed. It is to be found in the seed. Corenwinder found that in the pollen of flowers there is a considerable amount of organic phosphorus recovered as phosphoric acid in the ash of these minute organisms. In this respect pollen is analogous with the seminal fluid. Saussure and, later, Garreau, Professor of Botany at Lille, pointed out that the leaves of a tree give, on estivation, ashes more rich in phosphorus than at any other epoch of vegetation. If now we gradually ascend to the examination of animals, we find that their bones, their muscles, their nervous and cerebral substance, the fluids of their organism, blood, milk, urine, seminal fluid, are always and everywhere permeated with phosphorus. Intimately associated with organic substances, phosphorus abounds in the cerebral mass and the nervous system. One may almost say that it is organized. Combined with oxygen and lime it forms one of the important elements of the skeleton. Dissolved by the animal fluids, it is unceasingly carried from one point to the other of the individual, and if its total amount remains fixed, for a given animal, its molecule nevertheless displaced by solvent or vital actions is excreted, then replaced by a new molecule, brought by the digestive system. To remove phosphoric acid and lime from the diet and try to nourish an animal on purely nitrogenous principles is to attempt its life. The animal in this respect behaves like the plant (Bobierre). Thousands of analyses made of recent years by Thezard show that, amongst invalids, the elimination of phosphoric acid through the urine follows a progress parallel with that of the disease. The further the latter progresses the more does the phosphate content of the urine increase; in these conditions when the loss resulting from the elimination cannot be repaired by a diet appropriate to the needs of the individual, which has led to phosphoric acid being regarded as the vital element *par excellence*, the human organism perishes with frightful rapidity. According to Elie de Beaumont, a human skeleton weighs, on an average, 4·6 kg., say 10 lb., and assuming that human bones contain 53·04 per cent of phosphate of lime, a skeleton ought to con-

tain 2·440 kg., say 5¼ lb. But a human body weighs, on an average, 75 kg., say 165 lb.; deducting the weight of the skeleton there remains 70 kg., say 154 lb. of soft parts, which on incineration yield, like ox-beef, 1·5 per cent of ash entirely composed of phosphate of soda, potash or lime, and alkaline chlorides. The amount of phosphoric acid which they contain may be taken as equal to an amount of phosphate of lime equal to 80 per cent of the weight of the ash, or to 1·5 per cent of the weight of the soft parts multiplied by 0·8, say 840 grm. These 840 grm. added to the 2·440 kg. contained in bones, give a total of 3·28 kg. of phosphate of lime, say 1·439 kg. of phosphoric acid or 639 grm. of pure phosphorus. These figures show the importance of the rôle which phosphoric acid plays in the support of the globe. They ought to teach us also to use, with wise foresight, the stores of phosphoric acid with which bygone ages have endowed us, because, whatever may be the importance of the deposits now known and exploited, and even of those which may be discovered in the future, they are far from being inexhaustible; besides the danger of dispersion of phosphoric acid by default of restitution to the soil actually exists, more threatening for a future less distant than that of the dispersion of nitrogen and potash.

Properties of Phosphorus—(1) *Physical Properties.*—Phosphorus obtained by Scheele's method, i.e. by the distillation of phosphate of lime and charcoal, is a colourless yellow translucent body. It is found in commerce mainly as sticks. At the ordinary temperature it is soft like wax, brittle in the cold. It has the odour of garlic. Its density varies between 1·82 and 1·84. It is insoluble in water and in alcohol, very soluble in essential oils, ether, benzol, carbon disulphide, sulphur chloride, and phosphorus chloride.[1] Phosphorus melts at a temperature of 44·2° C. and forms a colourless, oily liquid; if melted phosphorus be rapidly cooled it is converted into a black mass with a metallic appearance; if, on the contrary, the molten mass be still further heated—up to a temperature of 250-260° C.—it is converted into a red modification which, at 280° C., reverts to the ordinary form. Phosphorus is highly poisonous. The absorption of a few centigrammes suffices to produce the death of a man by

[1] The solution of phosphorus in carbon disulphide was used by the Irish Fenians to burn the farms of their countrymen who were refractory to the Land League. This solution evaporates spontaneously and leaves phosphorus in a state of extreme division. The phosphorus then inflames spontaneously. If wooden objects be coated with a solution of Fenian fire nothing can prevent a conflagration. The solution of phosphorus in carbon disulphide, mixed with sulphur chloride, can be preserved well in close vessels but inflames with violence if a few drops of ammonia are allowed to fall thereon. This is the Lorraine fire of Nickles of 1869. Care must be taken to work in the open air on small quantities and to pour the ammonia by aid of a long tube. The new Lorraine fire of P. Guyot, 1871, is a solution of phosphorus in carbon disulphide to which sulphur bromide has been added. It inflames in 1 or 2 minutes after ammonia has been added.

the excitation of the nervous centres which it produces. Its antidote is spirits of turpentine. The vapours of phosphorus frequently respired induce necrosis of the bones, chiefly those of the face. The ordinary phosphorus industry and the manufacture of matches are amongst the most unhealthy of unsanitary trades. *Chemical Properties.*—(2) Ordinary phosphorus oxidizes slowly in the air, and this oxidation is accompanied by a phosphorescent glow, from which phosphorus takes its name. Its suffices, moreover, to cut it with a knife to inflame it, by the heat produced by the friction; that is why it should be cut under water. Chemically combined oxygen exercises on phosphorus the same oxidizing action as free oxygen. Water, which is a very stable compound of oxygen and hydrogen, is destroyed, though slowly, by this body with formation of phosphoric acid and phosphoretted hydrogen. The transformation is more rapid when the water is rendered alkaline by caustic potash, soda, or lime. Nitric acid oxidizes phosphorus very energetically, converting it mostly into phosphoric acid. Owing to its great affinity for oxygen, phosphorus is not found in nature in the free state, it is always met with as phosphoric acid combined with bases.

Oxygenated Compounds of Phosphorus.—Phosphorus forms with oxygen and hydrogen the following anhydrides and acids:—

	Anhydrides.	Acids.
Hypophosphorous acid		H_3PO_2
Phosphorous acid	P_2O_3	H_3PO_3
Phosphoric acid	P_2O_5	H_3PO_4

There are three phosphoric acids known, viz.:—

Metaphosphoric acid $H_2OP_2O_5 = HPO_3$
Pyrophosphoric acid $2H_2OP_2O_5 = H_4P_2O_7$
Orthophosphoric acid $3H_2OP_2O_5 = H_3PO_4$

Hypophosphorous acid is monobasic, that is to say, only one of its atoms of hydrogen can be replaced by a metallic atom. Phosphorous acid is dibasic, and phosphoric acid tribasic. There are, therefore, three phosphoric acids, which differ in the fact that one, two, or three atoms of H may be replaced by as many basic atoms. It is to Graham that we owe the discovery of their characteristic reactions. Metaphosphoric acid only gives one species of metaphosphate. Pyrophosphoric acid gives two species of pyrophosphates. Orthophosphoric acid gives three species of salts corresponding to the formulæ M_3PO_4; M_2HPO_4; MH_2PO_4. These acids are distinguished the one from the other by the following reaction: the meta acid gives a white precipitate, with barium chloride and silver nitrate, and coagulates a solution of albumen; the pyro acid gives no precipitate with barium chloride, gives a white precipitate with silver nitrate, and does not coagulate albumen; the ortho acid

gives no precipitate with barium chloride, gives a yellow precipitate with silver nitrate, and does not coagulate albumen.

Phosphoric Acid Anhydride, P_2O_5, is obtained by the combustion of phosphorus in a current of very dry air. It forms imponderable, highly deliquescent, white flocks. It dissolves in water with the hissing noise of red-hot iron. Hence its use to dry gases at temperatures at which sulphuric acid would be decomposed, and to prepare by dehydration certain acid anhydrides or certain organic compounds, nitriles for example. Heated to redness with charcoal it yields carbonic oxide and phosphorus.

Metaphosphoric Acid, HPO_3, is monobasic. It is prepared by hydrating the cold anhydride, by heating orthophosphoric acid to redness, or by calcining ammonium phosphate at a red heat. It is a vitreous substance, volatile at a red heat, very soluble in water, with which it combines to reproduce orthophosphoric acid. It is used to dry gases. The metaphosphates prepared by calcining monometallic orthophosphates are only partially reduced by charcoal.

Pyrophosphoric Acid is dibasic. It is prepared by subjecting orthophosphoric acid to prolonged heat at 200° C. Calcined, it gives metaphosphoric acid; with water it reproduces orthophosphoric acid. Pyrophosphates, prepared by calcining bi-metallic orthophosphates, or by heating phosphoric acid with an oxide, are reducible by charcoal.

As far as the manufacture of chemical manures is concerned, the only important modification to be borne in mind is the ordinary or orthophosphoric acid. However, pyrophosphoric acid is sometimes met with in phosphates that have been roasted to facilitate grinding, and metaphosphoric acid in superphosphates dried at too high a temperature.

Orthophosphoric Acid, H_3PO_4.—This, the ordinary phosphoric acid, is tribasic. It is obtained mixed with phosphorus, in the slow oxidation of phosphorus in moist air. It is prepared in the laboratory by oxidizing red phosphorus by the aid of heat with fifteen times its weight of nitric acid of 20 B. The reaction may be expressed thus: $3P + 5HNO_3 + 2H_2O = 3H_3PO_4 + 5NO$. The phosphorus is only added gradually and in small portions at a time. Orthophosphoric acid is produced, which remains in the retort, and a little nitrogen dioxide, which carries over some nitric acid. Care is therefore taken to redistil "cohobitate," until the whole of the phosphorus has disappeared; the residue is then evaporated in a platinum basin to expel all nitric acid and to convert any phosphorous acid which may have been formed into phosphoric acid, taking care not to exceed 188° C., otherwise pyrophosphoric acid will be obtained. Orthophosphoric acid is also produced by the action of hot water on metaphosphoric acid, by igniting hypophos-

phorous or phosphorous acids, or by the action of water in excess on pentachloride of phosphorus. In the concentrated state ordinary phosphoric acid forms a thick, inodorous, very acid, non-poisonous syrup, of density 1·88. It crystallizes with three molecules of water when evaporated under a bell jar over sulphuric acid. It is very soluble in water, and highly deliquescent. Under the action of heat, it is converted at about 213° C. into pyrophosphoric acid, and towards a red heat into metaphosphoric acid. It is reduced by red-hot charcoal, yielding phosphorus. It gives no precipitate with barium chloride, nor with perchloride of iron, nor with a solution of silver, nor with albumen. But if ammonia be cautiously added, barium chloride gives a brownish precipitate, and a solution of silver a yellow one ; both precipitates are soluble in acetic acid. A characteristic test for phosphoric acid is the production of the double phosphate of magnesium and ammonium, by "magnesia mixture," consisting of ammonia, magnesium chloride, and water. This precipitate is white and crystalline; it suffices to see it once not to confuse it with any other precipitate. A reagent which enables traces of phosphoric acid to be detected, consists of a nitric acid solution of ammonium molybdate. If the mixture of the two solutions be heated the liquid assumes a bright yellow coloration.[1] Ordinary phosphoric acid is a very stable compound. It displaces sulphuric and nitric acids from their compounds.

Phosphates of Lime.—It has just been seen that phosphoric acid is tribasic, i.e. it contains three atoms of hydrogen, replaceable by metals.

$PO\{^{OH}_{OH}_{OH}$	$PO\{^{OM}_{OH}_{OH}$	$PO\{^{OM}_{OM}_{OH}$	$PO\{^{OM}_{OM}_{OM}$
Orthophosphoric Acid	Monometallic Orthophosphate	Dimetallic Orthophosphate	Trimetallic Orthophosphate

When the hydrogen of phosphoric acid is replaced by calcium, a divalent element, three types of phosphates are obtained to which the commercial varieties of phosphatic manures correspond in a very characteristic fashion.

$PO\{^{OH}_{OH}_{O>Ca}$ $PO\{^{O>Ca}_{OH}_{OH}$	$PO\{^{O}_{O>Ca}_{O>Ca}$ $PO\{^{O>Ca}_{OH}_{OH}$	$PO\{^{O}_{O>Ca}_{O>Ca}$ $PO\{^{O>Ca}_{O}_{O>Ca}$
Monocalcic phosphate or acid phosphate of lime, $CaH_4(PO_4)_2$	Dicalcic phosphate or monacid phosphate of lime	Tricalcic phosphate, Neutral phosphate of lime, Tribasic phosphate of lime, $Ca_3(PO_4)_2$

[1] But ammonium molybdate in nitric acid solution gives a yellow coloration even in the absence of phosphoric acid. Unless there is a decided yellow pre-

Monocalcic phosphate or superphosphate is characterized by its complete solubility (*a*) in water, (*b*) in ammoniacal citrate of ammonia (aqueous solution of ammonium citrate with excess of ammonia), and (*c*) in strong mineral acids. The sole object of superphosphate manufacture is to convert the tricalcic phosphates of bones and mineral phosphates into monocalcic or acid phosphate, assimilable by plants. Dicalcic phosphate, or precipitated phosphate, is insoluble in water, but soluble in ammoniacal citrate of ammonia, and strong mineral acids. It is obtained in the treating of bones by hydrochloric acid, in the manufacture of gelatine (glue), as will be seen in the sequel. Tricalcic phosphate forms the chief mass of the substance of bones which resists combustion (bone ash), of phosphorites, of apatite, and of a great number of guanos. In the calcined state, or as apatite, it is insoluble in water, slightly soluble in water saturated with carbonic acid. It is completely soluble in nitric and hydrochloric acids, which convert it into monocalcic phosphate, displacing two-thirds of the lime to form, with it, calcium nitrate or calcium chloride. Sulphuric acid completely decomposes it into free phosphoric acid and sulphate of lime (gypsum). Phosphoric acid is precipitated from acid solutions, by excess of lime water, as a fine white powder, which is partly soluble in water, especially when it contains potassium sulphate, common salt, nitrate of soda, ammoniacal salts, or carbonic acid.

Phosphates of Ammonium, Sodium, etc.—Let us examine a few other phosphates of importance in manure manufacture:—

1. *Basic Phosphate of Ammonium*, $(NH_4)_3PO_4$, is a slightly soluble, very unstable salt, obtained by mixing syrupy phosphoric acid with excess of ammonia. Its aqueous solution exposed to the air loses one-third of its ammonia, and is converted into the monacid phosphate; heated, it loses a second third, and is then converted into the acid phosphate.

2. *Monacid Phosphate of Sodium* (*ordinary commercial phosphate of soda*, $Na_2HPO_4 + 12H_2O$) is contained in urine. It forms large crystals, which turn dull in the air, through loss of a portion of their water. Heat converts it into pyrophosphate by expulsion of water. It is prepared on the large scale by saturating crude phosphoric acid with soda to alkaline reaction and crystallizing.

3. *Monacid Phosphate of Ammonium and Sodium*, $NaNH_4HPO_4 + 4H_2O$.—This salt is prepared by dissolving ammonium chloride in a solution of ordinary phosphate of soda. Heat converts it into sodium metaphosphate, $NaPO_3$, with liberation of ammonia and water. Putrefying human urine yields a deposit of this salt. It forms crystals as clear as water, and is found in that state in

cipitate on warming gently, phosphoric acid may be taken as absent. Even a precipitate is no sign of the presence of phosphoric acid unless all traces of arsenic have previously been removed.—Tr.

guano, under the name of *stercorite*. Its solution on standing gives off ammonia.

4. *Monacid Phosphate of Ammonium* is, likewise, found in Peruvian guano. It is formed from the neutral salt through loss of ammonia. It has an alkaline reaction, like all monacid soluble phosphates. The acid phosphates of potassium, of sodium and of ammonium are still more soluble in water than the preceding. Their solutions turn red litmus paper blue.

5. *Magnesium Phosphates*—(1) *Basic Phosphate of Magnesium*, $Mg_3(PO_4)_2$, is found in small quantities in seeds. It is very soluble in acids; it is precipitated from its acid solution by ammonia as phosphate of ammonia and magnesia. (2) *Monacid Phosphate of Magnesium.*—This, like the corresponding lime compound, is a very soluble salt. (3) *Double Phosphate of Ammonium and Magnesium*, $NH_4MgPO_4 + 6H_2O$, is precipitated from solutions which contain at one and the same time phosphoric acid, magnesia salts and ammonia, as a white crystalline powder slightly soluble in water and almost insoluble in ammonia water. Ignited, it leaves a residue of pyrophosphate. This interesting compound was found in large crystals as clear as water in excavating the soil for the foundations of the church of St. Nicolas in Hamburg. The name of *struvite* was given to it. In this locality there was a cesspool, from which the matter spread into the peaty soil. As peat contains a large amount of ammoniacal salts, the phosphate of magnesia from the urine had formed the double phosphate of ammonia and magnesia, which remained in solution for a somewhat lengthened period in the ammoniacal salts in excess. By slow precipitation crystals were formed, some as large as a hazel nut. This same salt is met with in different varieties of guanos, but in much smaller crystals. Its formation is analogous to that which occurs in putrefying urine: the phosphate of magnesia is brought by the urine, the ammonia results from the putrefaction of the nitrogenous constituents of the guano.

6. *Phosphates of Iron.*—The basic phosphates of iron are widely distributed in nature, but their composition is very variable. They are formed wherever phosphates dissolved by the moisture in the soil come in contact with oxide of iron. In arable land, which as is well known always contains oxide of iron, a portion of the phosphoric acid is in all probability combined with that oxide. The phosphate of the protoxide of iron (ferrous phosphate) is formed in an analogous manner; it is only reduced to protoxide by decomposing organic matter. This product is found in large masses in certain peaty districts. A basic artificial phosphate is obtained by mixing perchloride of iron with excess of phosphate of soda. It possesses a yellowish colour, which turns brown on heating. But the compound so obtained is never pure,

and its composition never corresponds to definite proportions. The pure basic phosphate is obtained from the preceding by moistening it with pure syrupy phosphoric acid, and washing it with a great excess of water. The product so obtained remains white on ignition. It is soluble in hydrochloric acid, perchloride of iron, and in acetate of iron, and insoluble in acetic acid. The acid phosphate of iron is prepared by dissolving the freshly precipitated, air-dried, basic phosphate in pure, syrupy phosphoric acid. Properly prepared, and the water abstracted, the solution has an analogous composition to other acid phosphates; it is rose-red, and may be converted by means of a large excess of water into free phosphoric acid and basic phosphate. It likewise yields a precipitate on heating. Tartaric, citric, and other non-volatile organic acids prevent the formation of the precipitate; mineral acids only possess this property but imperfectly.

7. *The Phosphates of Alumina* behave in a general way like the phosphates of iron. Wavellite, a crystallized mineral phosphate, is a phosphate of alumina. Redonda phosphate, which forms an important deposit, consists chiefly of a compound of this nature.

The phosphates just described are met with in different phosphatic manures, natural or artificial. The majority of them, such as the alkaline and ammonium phosphates, are only represented in small proportions it is true; however, one cannot but acknowledge their vast importance from the point of view of the mobility of phosphoric acid in the soil, and in the organism. The only phosphates found in preponderating amount in manures are the phosphates of lime. The basic phosphates of lime are spread over numerous points of the globe; as will be seen further on considerable deposits of them exist which are wrought commercially. But these phosphates are more or less mixed with impurities, that is why they serve exclusively as raw material for the manufacture of phosphatic manures, properly so called, which are acid phosphates of lime, or *superphosphates*.

Moreover, various industries supply important quantities of basic phosphates, obtained as bye-products. They deliver them to manure manufacturers, who use them in making superphosphates, or they dispatch them direct to the farmers (basic slag).

CHAPTER II.

PRINCIPAL PHOSPHATE DEPOSITS.

I. France.—*Pas de Calais, Somme, Oise.*—In these departments the deposits of phosphates are met with in the Cretaceous formation, at three distinct levels in this formation. These are in ascending order. 1. The Gault, to which the Boulogne workings belong. The nodules found in these beds contain 20 per cent of phosphoric acid. 2. The Glauconian chalk, which forms the phosphate basin of Pernes and of Fauquemberg, with 25 per cent of phosphoric acid. 3. The Upper Chalk bed, characterized by *Belemnites quadratus*, the most important of all. The phosphate deposits of Orville, Beauval, and Hardivillers are on this horizon. In these workings phosphate rich in sand is found in pockets, in the upper chalk, below the clay or surface *bief* (? boulder clay). These pockets, which are wrought very energetically, are only of limited duration, and are in process of exhaustion. Besides the pockets of rich sand, there exist in the *Belemnites* chalk cliffs parts sufficiently rich in phosphate of lime to be worth extracting and treating by one of the enrichment processes to be described further on. This phosphatic chalk, called also "grey chalk" (*craie tuffeau*), etc., forms in certain points masses of considerable dimensions. The percentage does not exceed 38 to 40 per cent of tribasic phosphate of lime. Below 28 or 30 per cent of tribasic phosphate of lime, the chalks are mostly considered as of no industrial value. At Breteuil near Clermont, for example, an extremely important bed of this chalk with 32 per cent of tribasic phosphate is only partially exploited, the enriched product not exceeding 45 per cent of tribasic phosphate.

1. *Somme Phosphate.*—The presence of phosphatic chalk in the Somme was first observed by Buteaux as far back as 1849. On the other hand, M. de Mercy discovered in 1863 and 1867 two other similar deposits, the one at Hardivillers near Breteuil (Oise), the other at Hallencourt near Abbeville, Somme; he showed their analogy with that of Beauval, and classed them like the latter in the *Belemnites quadratus* chalk. The Beauval deposits were discovered in 1886 by two geologists, Merle and Poncin. The phosphatic sands of that locality, and its environs, are accumulated on the edges of pockets in the form of reversed cones excavated in a bed of chalk, filled with small brown-yellow grains of phosphate of lime situated at the base of the *Belemnites quadratus* chalk, and

resting on the *Micraster Coranguinum* white chalk. This formation is found therefore about the middle Senonian horizon. The phosphatiferous chalk is of a bright chamois colour and is known in the district under the name of grey chalk; its phosphoric acid content is from 10 to 15 per cent at the point of contact of the grey chalk and the white, *Micraster*, chalk. There is at Orville a discontinuous, almost horizontal bed of phosphatic nodules of a yellowish-white colour. Some are coloured black on the exterior, due to a bright coat which would appear to be manganese dioxide; they are rarely the size of a small nut and contain 70 to 80 per cent of tribasic phosphate. They are agglomerated by a gangue of white carbonate of lime. The phosphatic sands of the Somme contain a rather large quantity of the teeth of dogfish, which appear to have been preserved by their enamel. Neither fossils nor bones are found there, though they exist in the *Belemnites* chalk. At Orville, where the phosphatic chalk is separated from the *Micraster* chalk by a bed of nodules, no nodules come from this bed except from the bottom of pockets which descend below the grey chalk. At Beauval, where the bed of nodules is absent, there is only to be seen at the apex of the funnels granular hard parts somewhat rich in phosphoric acid. The amount of rich phosphatic sand in the deposits of the neighbourhood of Doullens, including that of Orville, which though situated in the department of the Pas de Calais ought to be considered as belonging geologically and commercially to the Somme group, has been estimated at about 1,500,000 tons. But these deposits are on the road to exhaustion. Soon, as Olry remarks, this region will re-enter the calm of olden times, and of this era of untold riches, beyond the fortunes acquired by certain privileged persons, there will only remain the memory aggrandized by tradition of a time of fever and of gain almost unique in French industrial annals. Some analyses of the phosphates of these deposits are now given.

TABLE II.—ANALYSES OF THREE DIFFERENT TYPES OF SOMME PHOSPHATES.

	75-80 Per cent Phosphate.	70-75 Per cent Phosphate.	60-65 Per cent Phosphate.
Moisture at 100° C.	0·59	1·42	2·80
Organic matter and combined water	1·45	—	—
Phosphoric acid	35·59	34·10	29·10
Lime	51·02	50·01	41·23
Oxide of iron	0·83	1·30	4·07
Oxide of alumina	0·56	0·23	
Magnesia and carbonic acid	9·17	—	CO_2 3·05
Insoluble in acids	0·79	1·60	8·55
Equal to tribasic phosphate of lime	77·69	74·44	63·53

TABLE III.—ANALYSIS OF AVERAGE SAMPLE OF A FIELD OF ORVILLE PHOSPHATE DRIED IN VACUO AT 98° C. DENSITY AT 16° C. 3·1307. (H. LASNE.)

	Per cent.
Sand and clay insoluble in hydrochloric acid	1·36
Organic matter and water volatile at a red heat	3·40
Soluble silica	0·47
Carbonic acid	3·70
Sulphuric acid (SO_3)	0·75
Phosphoric acid	33·86
Lime	47·54
Magnesia	1·20
Alumina	1·70
Oxide of iron (Fe_2O_3)	1·22
Calcium fluoride	4·65
	99·85

TABLE IV.—BEAUVAL PHOSPHATE DEPOSIT. ANALYSIS MADE BY NANTIER AT THE DATE OF DISCOVERY.

	Per cent.
Phosphoric acid	30·89
Lime	45·33
Carbonic acid	2·04
Fluorine	1·60
Sulphuric acid	1·84
Peroxide of iron	0·50
Alumina	0·32
Magnesia	0·16
Silica	0·38
Organic matter	2·26
Water	15·99
	101·31

Which corresponds before drying to a content of—

Phosphate of lime	67·43
Carbonate of lime	4·60
Calcium fluoride	3·24
„ sulphate	1·43

Drying raises the phosphate of lime content of this product to 80 per cent.

2. *Pas de Calais Phosphates.*—The phosphate bed situated between the Gault and the Greensand extends over vast tracts. In the Pas de Calais it forms the prolongation of deposits recognized in England as of the same stratigraphical horizon in the counties of Kent, Sussex, and Surrey. There is reason also to assimilate it with the geological horizon exploited in the Ardennes and in the Meuse. It was in the Pas de Calais at Wissant that Berthier first discovered in France the presence of phosphate of lime in nodules,

amongst pyrites being wrought at the base of the Gault clay for the manufacture of green vitriol. The stony matter mixed with the pyrites yielded on analysis 57·4 per cent of phosphate of lime. Later on, Dr. Turner discovered phosphatic nodules in the Gault at Lottinghem. Finally, the investigations of Meugy, Desailly, and de Molon in the Ardennes, from 1852 to 1856, having drawn public attention to the phosphates of the Greensand, these were not long in being exploited in the Pas de Calais, which has since become one of the principal centres of production. The nodules or lumps of this bed to which the name of *coquins* are still given, are generally round in form smooth or mamillary. Their size varies from that of a nut to that of the fist. They are grey or brown on the surface, with sometimes a bluish, sometimes a greenish cast. In the interior they are dark brown or black. Some of them are penetrated by iron pyrites, glauconite, gypsum, or quartz. In the Pas de Calais they are consolidated by an argillaceous cement containing 25 per cent of glauconitic sand, which makes a sort of conglomerate, of which the mass is formed of 35 to 40 per cent of nodules, and 60 to 65 per cent of argillo-silicious matter; sometimes shells, woody fragments, coniferous fruits, dog-fish teeth, fish bones, crystals of carbonate of lime, are found therein. The bed of nodules is fairly regular; its thickness varies from 6 to 8 inches.

Chemical Composition of the Pas de Calais Nodules.—The chemical composition of the nodules varies, as two analyses by Delattre show.[1] It follows from these analyses that the Gault nodules consist essentially in the Pas de Calais of phosphate of lime, carbonate of lime, fluoride of calcium, clay, sand and glauconite, the whole associated with a certain proportion of organic matter, about 0·10 per cent of nitrogen (ammoniacal); the glauconite brings also a certain amount of potash. The extent believed to be exploitable in the bed situated at the base of the Gault clay is estimated at 600 hectares, say 1500 acres, in the Boulogne district. At the base of the Cenomanien formation or Glauconitic chalk, there are in certain localities in the Pas de Calais workable beds of phosphate of lime. Also, in the district of Audincthem, Dennebrœucq and Reclinghem, and in that of Fléchin, Febvin-Palfart, Nédonchelle, Bailleul-les-Pernes, Aumerval and Pernes-en-Artois, at a short distance from the coal basin. The bed of phosphate has a thickness of 5 to 10 inches; the nodules are greenish, rather large and agglomerated by a sandy clay. They are more friable than those of the Boulogne district, and yield, on washing, about 25 per cent of by-products. They titrate from 50 to 60 per cent of phosphate of lime.

[1] See Table V, p. 18.

TABLE V.—ANALYSES OF PAS DE CALAIS PHOSPHATES.

	Phosphate.	
	Nabringhem.	*Fiennes.*
Moisture at 100° C.	1·40	1·40
Matter volatile at a dull red heat	5·60	5 30
Phosphoric acid (1)	23·52	20·72
Sulphuric acid	1·06	0·89
Carbonic acid (2)	4·30	4·20
Fluorine (3)	1·90	1·83
Lime	34·77	33·71
Magnesia	0·04	traces
Alumina	3·53	3·25
Oxide of iron	3·19	3·15
Silica	20·60	25·20
	99·91	99·65
Deduct oxygen equal to the fluorine	0·80	0·77
	99·11	98 88
Undetermined and loss	0·89	1·12
Total	100·00	100·00
(1) Equal to tribasic phosphate of lime	51·36	45·23
(2) Equal to carbonate of lime	9·77	9·54
(3) Equal to calcium fluoride	3·90	3·76

3. *Meuse, Ardennes and La Marne Phosphates.*—The phosphates exploited in this district come almost entirely from the base of the cretaceous (Greensand). This formation forms almost a continuous zone which extends over 187 miles from the department of Ardennes as far as Yonne, crossing those of la Meuse, la Marne and the Haute Marne and Aube. It consists mostly of one, sometimes of two beds of nodules of phosphate of lime, of a thickness of 6 to 8 inches, but in certain districts it thins out so much as to be no longer workable, the phosphate disappearing entirely, or not existing in sufficient quantity. The existence of Greensand nodules in *les Ardennes* was first pointed out in 1842 by Sauvage and Bauvignier, and their chemical composition was determined in 1852 and 1853 by Meugy. The first extraction works were undertaken by Desailly in 1856 and are still in existence. But, in a general way, the works are very unstable, the sheds removing as soon as the dead ground becomes too powerful, or the nodule bed thins out. The Meuse nodules have much the same appearance and composition as those of the Boulogne district; their phosphoric acid content generally varies from 14 to 20 per cent; it rarely exceeds the latter limit. Sometimes they are small, sometimes they reach or exceed the size of an ostrich's egg; they exhibit irregular contours into the spaces between which a green argillaceous sand penetrates, which forces them to be broken in bulk so as to clean them. At other times the phosphate of lime instead of being

in lumps isolated in the sand assumes the form of a conglomerate with a sandy cement known under the name of *Crassins*. These Crassins are very difficult to clean and yield products poor in phosphoric acid. A sample of nodules from the neighbourhood of Grandpré, analyzed at the *Bureau d'Essais de l'École des Mines*, had the following composition :—

TABLE VI.—ANALYSIS OF MEUSE PHOSPHATES.

	Per cent.
Clay and quartz	14·0
Alumina and oxide of iron	25 5
Lime	32·5
Phosphoric acid	17·5
Carbonic acid	9 0
Total	98 5

Other and more complete analyses have been published by Delattre. The following are quoted :—

TABLE VII.—ANALYSES OF VARIOUS PHOSPHATES IN THE MEUSE, ARDENNES, ETC., DISTRICTS. (DELATTRE.)

	Source of the Phosphates.			
	Les Islettis.	Dombasle.	Grandpré.	Chesnors or Boncourt.
Moisture at 100° C.	1·90	1·75	2·20	2·15
Matter volatile at a red heat	5·05	4·80	4·55	3·75
Phosphoric acid	18·74	18·23	19·57	16·69
Sulphuric acid	1·20	0·79	0·85	0·79
Carbonic acid	4·80	4·50	5·80	4·70
Fluorine	1·43	1 31	1·66	1·75
Lime	29·23	27·66	31·81	26·88
Magnesia	0·39	traces	0·36	traces
Alumina	2·57	2·30	3·36	2·47
Oxide of iron	5·46	5·83	4·89	3·77
Silica	28·74	32·06	24·80	37·16
	99·56	[1] 99·25	99·95	100·11
Deduct oxygen equal to fluorine	0·62	0·55	0·69	0·75
	98·94	98·70	99·16	99·38
Undetermined and loss	1·06	1·30	0·84	0·62
Totals	100·00	100·00	100·00	100·00
Equal to phosphate of lime	40·90	39·79	42·73	36·43
Equal to carbonate of lime	10·90	10·22	13·18	10·68
Equal to calcium fluoride	3·05	2·70	3·40	3·59

[1] Is made to total to 99·25 in original French, but only adds to 99·23.

TABLE VIII.—ANALYSIS OF ARDENNES NODULES. (MARET AND DELATTRE.)

	Per cent.
Moisture	2·20
Organic matter	3·35
Carbonic acid	4·60
Sulphuric acid	0·75
Phosphoric acid	18·35
Fluorine	1·37
Lime	27·52
Magnesia	0·08
Alumina	2·37
Oxide of iron	5·20
Potash soluble in nitric acid	0·99
Silica	32·42
	99·20
Deduct oxygen equal to fluorine	0·57
	98·63
Undetermined and loss	1·37
	100·00
Carbonate of lime	10·45
Phosphate of lime	40·08
Calcium fluoride	2·81
Nitrogen	0·084

These analyses show that the Meuse and Ardennes nodules are similar in composition to those of Boulonnais and the neighbourhood of Pernes-en-Artois, which is quite natural, both being of the same origin and situated at almost the same geological horizon.

4. *Côte d'Or Phosphates.*—As far back as 1822, De Bonnard discovered near St. Thibault (Côte d'Or), in a cutting of the Burgundy Canal, greyish-white nodules which contained, according to an analysis by Berthier, 74 per cent of phosphate of lime. These nodules associated with grains of ammonite were impasted in a mass of brown clay, but at that period but little importance was attached to the discovery, and it was only in 1872 that Collenot re-discovered them in excavations made on the plan of the railway from Cravant to Laumes. He collected samples which Georges Ville found to contain 60 to 64 per cent of tribasic phosphate. In 1873-4 this formation was examined by Poncin, who immediately profited thereby. It was thus that towards the end of 1876 the phosphate works of Auxois came into being. The horizon exploited belongs to the Lower Lias of Burgundy; it is situated towards the summit of the gryphesis *arquées* (? gryphea incurva) limestone zone with *Ammonites Stellaris*. Towards the top this limestone is rich in soft, almost friable phosphatic nodules, which are enclosed in the marly mass, the whole forming a mixture, the phosphate content of which varies from 30 to 45 per cent. The phosphatic

limestone is known in the district as "calf's liver" (*foie de veau*). It is not workable in the natural state owing to its irregular composition, but over large stretches the gryphea limestone has been altered and dissolved by the surface water which has left *in situ*, as an insoluble residue, an argillo-ferruginous mud in which the phosphate bed is represented by a layer of nodules cemented by a gangue of a similar nature. In such conditions the phosphate nodules may be exploited, for it is easy to separate them from the substance with which they are mixed, by drying and sorting, followed by washing. The thickness of the bed varies from 10 to 20 cm. (4 to 8 inches), but this thickness sometimes reaches 30 and even 40 cm. (12 to 16 inches), whilst elsewhere the bed is lost completely and ceases to be exploitable. The nodules are irregular in shape and greyish-white or yellowish; they are soft, almost friable. Their fracture shows grey spots with some blackish veins. Their size varies from that of a hazel nut to that of the fist. They generally have rounded edges, exhibiting a more or less angular shape. The mass contains 20 to 25 per cent of nodules, and 75 to 80 per cent of mud. The thickness of the mud or clinker which covers the bed is very variable, $\frac{1}{2}$ to 3 metres (20 to 120 inches) at the most. The Auxois nodules contain 27 to 30 per cent of phosphoric acid, equal to 59 to 65 per cent of tribasic phosphate of lime. The following are the results of three analyses by Delattre:—

TABLE IX.—ANALYSES OF AUXOIS PHOSPHATES. (DELATTRE.)

	I. Per cent	II. Per cent	III. Per cent
Water at 100	2·10	1·60	1·20
Matter volatile at a red heat	2·10	2·50	2·50
Phosphoric acid	27·06	28·59	29·71
Sulphuric acid	traces	0·17	0·17
Carbonic acid	2·60	2·50	2·20
Fluorine	1·75	2·40	1·55
Lime	35·84	37·92	38·08
Magnesia	traces	0·18	traces
Alumina	2·40	2·47	2·63
Oxide of iron	7·35	7·24	7·45
Silica	18·00	14·40	14·20
	99·20	99·97	[1] 99·49
Deduct oxygen equal to the fluorine	0·75	1·01	0·65
	98·47	98·96	98·84
Undetermined matter and loss	1·53	1·04	1·16
Totals	100·00	100·00	100·00
Equal to phosphate of lime	59·07	62·41	64·85
Equal to carbonate of lime	5·90	5·68	5·00
Equal to calcium fluoride	3·59	4·94	3·16

[1] Totals to 99·69.

According to the French mining statistics of 1887, the approximate extent of the Côte d'Or phosphate deposits is estimated at 5000 hectares (12,500 acres), containing 1,500,000 tons of that product.

5. *Cher Phosphate.*—Beyond the districts described, a bed with nodules 15 cm. to 20 cm., say 6 to 8 inches thick, situated in the upper Albin, has lately been wrought in the department of Cher. These nodules, of a yellowish-white colour and sometimes loaded with silex, are associated with white quartzose sand and gravels in the proportion of about one-third. They only contain 14 to 16 per cent of phosphoric acid. They are hard, and hence difficult to grind, and their freight was heavy owing to the great distance from a railway station. They were wrought exclusively in the open air, within the radius of Vailly sur Saldre, then after having been washed on the spot, they were ground and dispatched. The irregularity of the deposit, the poor phosphoric acid content of the nodules, their great hardness and the heavy cost of freight, rendered these workings expensive, and they were abandoned.

6. *Quercy Phosphates* (*Lot and Neighbouring Departments*).—Phosphate deposits occur over a wide area in Quercy. The phosphate occurs in concretions in the form of big pockets or vertical veins in the limestone (*causses*) belonging to the lower oligocene. They are only found in the high limestone plateaus which have been traversed by the fresh waters of the eocene, and almost always in the immediate neighbourhood of tertiary *ilots* (outliers) left on the spot. These outliers never exceed 350 metres (1148 feet) high, and it would be useless to seek for phosphate pockets on Jurassic plateaus of greater altitude. The pockets are very variable; some have a diameter of 35 metres (115 feet), others are crevasses of 3 to 6 metres (10 to 20 feet), following a straight line over 90 metres (say 300 feet). All the known pockets end in a point at the bottom, and widen near the surface. The irregular nature of these deposits seems to form an obstacle to their development. Their high phosphoric acid content seems to have led to a multiplication of badly organized works which ceased to be self-supporting when it was necessary to go lower down. These phosphates are chiefly used in the manufacture of superphosphates to increase the percentage of poor phosphates, so as to bring them to the commercial standard of 15 to 16 per cent of phosphoric acid soluble in ammonium citrate. Their average composition is as follows:—

TABLE X.—ANALYSIS OF QUERCY PHOSPHATES.

	Per cent.
Water and organic matter	5·31
Phosphoric acid	35·33
Lime	48·72
Carbonic acid	3·42
Sulphuric acid	—
Fluorine	—
Magnesia	0·08
Oxide of iron	2·24
Alumina	2·78
Insoluble	2·12
	100·00

7. *Gard and Ardeche Phosphates.*—The Gard deposits are chiefly phosphorites, the formation of which has been contemporaneous with those of Quercy. They are found in irregular excavations amongst the compact limestone of the Urgonian age. The workings are underground. The chief producing centres are on the lands of the communes of Tavel and Lirac. There are also deposits of nodules in Saint-Julien-de-Peyrolas and Salazac, also in the department of Ardeche at Saut-de-l'Eygue, la Rousette, Beyne, etc. Production almost nil.

8. *Drôme and Isère Phosphates.*—In Drôme they chiefly work the Greensand nodules at Saint-Paul-Trois-Chateaux in the district of Montelimar. The content of these nodules does not exceed 55 per cent of tribasic phosphate of lime; it averages 45 per cent. The workings are unimportant, are solely in the open air, and consist of screening the nodules and scrubbing them in water to separate adhering sand. In Isère there are fossiliferous and phosphatic beds (Gault) of great regularity, but the rock is sometimes so compact that the nodules cannot be washed and enriched by simple economic means, such as screening and scrubbing, which are the only methods that can be applied to material so poor in value.

9. *Pyrenees or Ariège Phosphates.*—These phosphates, described by Dr. Levat in a memoir presented to the Academy of Sciences, form a vast bed developed in the valleys of Bonnes, Luchon, Salat, in the neighbourhood of Prades, ascending towards the north in les Corbières as far as the environs of Cannes. Pyrenees or Ariège phosphates have a brilliant black appearance recalling that of anthracite. The composition of the bed is characterized in its rich parts by numerous black, brilliant, usually flattened nodules consisting of almost pure phosphate of lime and testing 65 to 75 per cent of tribasic phosphate of lime. The gangue encrusting these nodules is itself phosphatic. Moreover, there has been found in it an important amount of organic matter containing organic nitrogen in the proportion of 11 lb. per ton. The extent of the bed reaches 8 to 10 metres (26 to 33 feet). The nodules are concentrated sometimes on the roof, sometimes on the wall of the deposit.

II. Belgium.—About 1874, Cornet discovered at Mesvin and at Ciply near Mons, below the landenien sands, a bed of 8 to 10 metres thick of brownish, friable, slightly coherent chalk containing 75 per cent of brown grains of carbonate and phosphate of lime, the largest of which are not bigger than a pin's head. This speckled chalk, known in the district as brown chalk (*craie brune*), contains 25 to 30 per cent of tribasic phosphate, with a slight enrichment at the base. It occurs at a higher level than the Beauval chalk. In the upper part it exhibits pockets, in which there are found masses of pudding-stone called *poudingue de la Malogne*, consisting of brown coloured nodules containing 50 per cent of phosphate, cemented

together by a calcareous paste. These nodules have an analogous composition with the brown grains. The calcareous tufa of Maestricht, itself phosphatic, rests on them. Other pockets, containing a chestnut-coloured phosphatic sand, like a highly ferruginous sand, tests 60 per cent of tribasic phosphate. This sand, which coats the sides of the excavations, is only about 30 cm., say 12 inches thick. It consists of the same small phosphatic grains that are met with in the brown chalk. The phosphatic chalk of Mesvin and Ciply, like that of Somme, is not commercially utilizable, but its extreme friability, and the facility with which the phosphatic grains are detachable from their chalky envelope, enable it to be enriched and to bring its content up to 50 and even 60 per cent of phosphate. It suffices to pulverize it and to submit it afterwards to an ascending current of air which removes the chalk dust and leaves the small heavier phosphatic grains, or to roast it slightly and to wash it in mechanical preparation plant. Other important phosphatic deposits occur in the district of Liége, at Rocour, Vottem, Hesbaye, on the right bank of the Meuse. It likewise occurs at Liers, Voroux, Milmort, Ans and Montéguée.

TABLE XI.—ANALYSES OF CIPLY PHOSPHATES.

	I.	II.	III.	IV.
Water	0·65	0·30	—	1·40
Organic matter	3·00	2·50	2·12	1·90
Phosphoric acid	18·68	22·14	24·69	26·29
Sulphuric acid	0·01	—	—	1·61
Lime	49·90	50·72	50·31	51·98
Carbonic acid	18·40	15·70	15·06	12·80
Magnesia	0·59	—	—	0·67
Oxide of iron and alumina	2·28	1·72	1·31	0·86
Insoluble	5·20	3·30	1·23	0·74
Undetermined	1·29	3·62	5·28	1·75
Totals	100·00	100·00	100·00	100·00
Equal to tribasic phosphate of lime	40·72	48·25	53·82	57·39
Equal to carbonate of lime	41·81	35·64	34·24	29·09

TABLE XII.—ANALYSES OF LIÉGE PHOSPHATES.

	I. *Per cent.*	II. *Per cent.*
Water	0·93	0·85
Chemically combined water	2·83	2·53
Phosphoric acid	27·20	25·08
Carbonic acid	3·10	3·00
Soluble silica	0·80	0·75
Lime	40·64	38·01
Magnesia	0·79	0·81
Oxide of iron and alumina	2·39	3·30
Calcium fluoride, calcium sulphate, etc.	5·93	4·40
Insoluble	15·34	21·27

III. England.—True coprolites or fossil excrements rich in phosphate of lime in the form of more or less round lumps, 6 to 20 cm. (2½ to 8 inches) in diameter, are found in England in the Lias marls, chiefly at Lyme Regis. The interior is earthy like hardened clay, but amongst these there can be readily distinguished the teeth and the bones of the fishes and reptiles which served as food to the saurians of the epoch such as the ichthyosaurus, the pleiosaurus and the teleosaurus. Coprolites have been found at the mouth of the Severn near Bristol.

TABLE XIII.—ANALYSES OF LYME REGIS COPROLITES.
(THOMPSON HERAPATH.)

	I. *Per cent.*	II. *Per cent.*
Water	6·182	2·976
Organic matter		2·001
Sodium chloride and sulphate	traces	—
Carbonate of lime	23·674	28·121
Carbonate of magnesia	—	0·423
Sulphate of lime	1·077	0·026
Phosphate of lime	60·769	53·996
Phosphate of magnesia	traces	
Phosphate of iron	4·057	6·182
Phosphate of alumina	traces	1·276
Ferric oxide	1·994	—
Alumina	traces	—
Silica, calcium fluoride, and loss	1·552	0·738
	100·009 [1]	100·000 [2]
Nitrogen	0·082	Undetermined
Density	2·700	2·799

TABLE XIV.—ANALYSIS OF CAMBRIDGE COPROLITES.

	Per cent.
Moisture	8·00
Organic matter	3·00
Silica	9·00
Phosphate of lime	77·70
Carbonate of lime	2·30
	100·00

TABLE XV.—ANALYSIS OF SUFFOLK COPROLITES.

	Per cent.
Combined water	10·00
Sand oxide of iron	21·00
Carbonate of lime	10·00
Phosphate of lime	56·00
Calcium fluoride sulphates and alkaline chlorides	3·00
	100·00

[1] Totals to 99·305. [2] Totals to 95·759.

As far back as 1848 antediluvian bones were dug out of the Suffolk and Norfolk *Crag*. The upper Norfolk Crag contains fossil bones of the elephant, rhinoceros, ox, etc. They are found mixed with sand and gravel at a depth of 70 to 80 cm. (27 to 31 inches). The samples from the bone bed in the neighbourhood of Sutton (Suffolk) are sometimes spongy and friable, sometimes fibrous and resistant. The latter readily take a fine polish, and their porosity can only be seen under the microscope. Their analysis gives the following figures:—

TABLE XVI.—ANALYSES OF FOSSIL BONES FROM SUTTON BONE BED.

	I.	II.
	Per cent.	*Per cent.*
Water extracted at 150° C. to 170° C.	3·361	2·912
Water and organic matter volatile at a red heat	4·351	3·361
Carbonate of lime	27·400	26·800
Carbonate of magnesia	0·371	0·286
Sulphate of lime	0·514	traces
Phosphate of lime combined with a little phosphate of magnesia	49·632	59·966
Phosphate of iron	6·600	4·800
Phosphate of alumina	3·400	4·638
Calcium fluoride	3·617	undetermined
Silica	0·626	0·098
	99·872	99·861
Nitrogen in 100 parts	0·1244	undetermined

Three other samples from the same locality intended for superphosphate manufacture, yielded 58·61 and 62 per cent of tribasic phosphate of lime. Besides these deposits of phosphorites, resulting from the burying of bones, phosphorites are also found in the county of Suffolk, at Felixtowe, Sutton and Walton; these deposits are 20 inches deep. The phosphorites occur there as brilliant black nodules, exceedingly hard, and were formerly used as pebbles for road-making. Their composition is as follows:—

TABLE XVII.—ANALYSES OF SUFFOLK, ETC., COPROLITES.

	Per cent.	*Per cent.*
Water and organic matter	4·0	—
Tricalcic phosphate	70·9	54
Carbonate of lime	10·28	10
Silica	5·79	—
Oxide of iron	—	5
Oxide of alumina	—	4
Fluorine	—	3

Finally, deposits of pseudo coprolites are found in the Welsh, Cambrian and Silurian at Mowdry, Pennyganedd, and at Beroin.

But the English superphosphate industry is almost entirely stopped, owing to the competition of other countries that possess more readily workable deposits. (See footnote p. 5 and context.)

IV. Sweden and Norway.—*Sweden.* Apatite with 36 to 41 per cent P_2O_5 is found in quartz at Horesjobera.

Norway.—In the Kragero schists, near Christiania, likewise in the granite and gneiss, crystalline apatite is met with rarely in crystals. Its colour is yellowish-white or greenish-grey or red. The crystals have the following composition:—

TABLE XVIII.—ANALYSIS OF NORWEGIAN APATITE (CRYSTALS).

	Per cent.	
Water	0·14	
Loss on ignition	0·27	
Phosphoric acid	39·44	= 86·10 $Ca_3P_2O_8$.
Lime	50·90	of which 2·28 is free lime.
Magnesia	0·64	
Oxide of iron	0·51	
Oxide of alumina	0·86	
Carbonic acid	0·15	
Sulphuric acid	0·12	
Chlorine	2·62	
Insoluble	3·62	

V. Germany.—Germany possesses almost no deposits of phosphate of lime industrially utilizable, and the recent geological examinations that have been made have hardly given any result.

VI. Austria-Hungary.—Deposits of poor phosphates exist in Bohemia, at Kostic and at Teplitz, the composition of which is as follows:—

TABLE XIX.—ANALYSIS OF BOHEMIAN PHOSPHATES.

	Per cent.
Phosphoric acid	15·15
Lime	32·62
Carbonic acid	12·95
Sulphuric acid	0·82
Calcium fluoride	3·51
Magnesia	1·04
Oxides of iron and alumina	5·17
Silica	2·14
Sand	26·14

Moreover, vast deposits of phosphorite are found in Galicia and Bukovina, which are connected with those of Central Russia, as will be seen further on.

VII. Russia.—There are two deposits of phosphorite in Russia of considerable extent, one of which, part of Podolia, 500,000 hectares (1,250,000 acres), and of Bessarabia, 70,000 hectares (175,000 acres), extends into Austria. Its most important centre is in the basin of the Dneister, between St. Urzica and Nozileu. The

phosphorite is found as nodules with a smooth and polished surface, rarely rugose or exfoliated, sometimes greasy to the touch and resembling polished cast-iron, 2 to 2½ inches in diameter; some are 8 inches in diameter. Their composition is as follows:—

TABLE XX.—ANALYSIS OF RUSSIAN PHOSPHORITE NODULES.

	Per cent.
Phosphate of lime	75·00
Carbonate of lime up to	12·23
Calcium fluoride	6·98
Sulphate of lime	1·60
Phosphate of magnesia up to	1·30
Oxide of iron and alumina	5·00
Organic matter	1·00

The richest and most extensive phosphate deposits are those of Central Russia. They occur chiefly in the governments of Podolsk, Kostromo, Smolensk, Koursk, Woronesch, Simbirsk, Tambow, and on the banks of the Volga, from which they trend towards the West as far as Niemen; they occupy a surface of 20,000,000 hectares (50,000,000 acres). The richest deposits consist in part of phosphate of lime, mixed with organic matter. According to a recent announcement it has been found that the building-stone used in the whole district is nothing but phosphate of lime. That is a highly interesting fact. The phosphorite contains:—

TABLE XXI.—ANALYSIS OF CENTRAL RUSSIA PHOSPHORITE.

	Per cent.
Water	5·10
Phosphoric acid	27·45
Lime	43·00
Carbonic acid	4·60
Oxide of iron	3·40
Oxide of alumina	1·09
Sulphuric acid	1·04
Fluorine	0·47
Silica	13·82

These immense deposits are not utilized. They are to all appearance destined to form the reserve from which Europe will draw when the deposits now being used up will be exhausted.

VIII. Spain.—There exist in the province of Estremadura extensive phosphate deposits, forming well-defined veins. At Logrosan the veins occupy a space of 12 to 20 sq. miles, they traverse the granite and the Silurian schists and only contain phosphate and quartz. The phosphate is apatite. It occurs as regular, generally dull hexagonal prisms of a yellowish or greenish colour, and unequal. It is found in its gangue first as more or less voluminous, crystalline fragments of 0·2 to 1 inch in length, then as crystals almost invisible to the naked eye, and distributed

through the paste of the rock. The Caceres deposits are more extensive, but the material is less rich in phosphoric acid. The veins traverse a compact limestone regarded as Devonian, and disperse themselves in the subjacent schists with thinning-out zones in contact. Phosphate veins also occur in the Silurian schists, which extend to the north of Alcantara, province of Caceres, of Badajoz, Elvas, Zarza Mayor, Albala, Montanchez, Majadas, Malpartida, Ceclavin, as far as Portalegre and Morvao in Portugal. The size of the veins varies from 20 cm. (8 inches) to 8 metres (25 feet). The phosphate and the containing rock are of the same nature as at Logrosan. The composition of Estremadura phosphate varies very considerably, as the very complete analyses of Schucht reproduced here show. (See also p. 5.)

TABLE XXI. (A).—ANALYSES OF SAMPLES OF ESTRAMADURA PHOSPHATES.

	Apatite extracted from Granite.		Phosphorite extracted from Granite.	Phosphorite Fibrous Earthy.		Phosphorite Scaly extracted from Limestone.	Phosphorite Earthy extracted from Limestone.
	Crystallized.	Crystalline.		Extracted from Schist.	Extracted from Limestone.		
Water . . .	—	—	0·25	0·15	0·05	0·85	0·90
Tricalcic phosphate .	93·82	89·68	78·16	87·21	74 40	80·77	79·46
Calcium fluoride .	5·44	5·38	2·18	8·00	3·08	1·03	4·53
Calcium chloride	0·31	—	0·16	—	—	traces	0·05
Carbonate of lime .	—	—	11·30	1·16	20·45	17·00	13·64
Sulphate of lime .	—	—	0·92	traces	traces	traces	traces
Silicic acid . .	0·30	1·90	5·60	2·00	1·10	0·10	0·20
Oxide of iron . .	—	1·15	1·10	0·84	0·50	0·08	0·90
Oxide of alumina .	—	1·30	traces	traces	—	—	—
Manganese dioxide .	—	0·39	traces	traces	traces	—	traces
Undetermined . .	0·13	0·15	0·34	0·64	0·42	0·17	0·33

IX. North America.—There are four centres of phosphate production in North America, viz. Canada, South Carolina, Florida, Tennessee. In addition to these, deposits of less importance occur in North Carolina, Pennsylvania, Massachusetts, Indiana, Kentucky, and Alabama.

Canada.—Deposits of apatite, crystallized in pockets and in veins, are wrought in Canada. The pockets of apatite are met with in beds of pyroxenit of variable magnitude but of great regularity in stratified conformable layers in the gneiss. The paleozoic limestones on which this gneiss lies are of the Laurentian age. The gneiss is itself pierced by numerous crystals of apatite. Apatite is

found in the province of Quebec, at Templeton, Buckingham, Portland, Egonville, Lievre-river; in the province of Ontario, at Leeds, Lamarck, Fontenac, Addington, Kingston, Perth and Renfrew County. The most important deposits are those of North Burgess, South Burgess, and North Emsley in Lawrence County.

The utilization of Canadian phosphates is embarrassed not only by the depression more or less transitory in the price of the goods, but further and still more by the irregular mode of occurrence of the deposit, and the obligation created by the dearness of freights and commercial customs, of only regarding as marketable and fit for export products containing 80 per cent of tribasic phosphate. Now this content cannot be secured except at great expense, and an enormous waste of low content material unutilizable, which is piled up on the outskirts of the mines. In fact, every mineral with less than 60 per cent is of no value in Canada, as not being capable of paying for the freight. Attempts have been made with the washing processes, with the result that certain deliveries have tested 87·83 of tribasic phosphate of lime. That is the highest figure attained in Canada. [Working has ceased for some years.—Tr.]

South Carolina.—The South Carolina phosphate deposits occur in Miocene strata from the Charleston basin as far as North Carolina, Georgia, and Florida. They are very extensive, and the nodules of phosphorite extracted therefrom are very analogous with those which exist in Central Russia and in the London Basin. They were discovered in 1869, i.e. long before the other North American deposits. The Carolina deposits extend along the coast with a breadth of 10 to 45 miles from the source of the River Wando and from the eastern arm of the River Cooper, which both flow into the Atlantic at Charleston, as far as the sources of Broad River. They are often found on the surface of the ground. At other times they are covered with sand and clay deposited by diluvial water. The rock phosphate is distinguished from the river phosphate (*Land Phosphate* and *River Phosphate*). The first is usually found 10 feet from the surface, the second on or under the bed of the rivers. Their colour varies according to their origin. That of the rock phosphate is yellowish or pale grey. River phosphates are black owing to presence of organic matter. The phosphorite occurs as nodules or balls, with a rugose surface, and smooth or pitted, sometimes shining as if enamelled. It is often mixed with shells, petrified bones, the teeth of terrestrial and marine animals. The diameter of the lumps varies from a few centimetres to 1 metre. Before the discovery of the Florida phosphates, the South Carolina deposits furnished about one-fifth of the world's consumption. Their product was perfectly suitable for making superphosphates with 13 per cent of phosphoric acid = 28·4 per cent soluble phosphate. The annual export amounted to 150,000 tons. But since

1890, Florida has not ceased to increase its production, and the low price caused thereby has led a certain number of those engaged in the industry in Carolina to stop work. Since that time the Carolina production has continued to diminish. The average composition of South Carolina nodules is the following, by Dr. C. W. Shepard of Charleston :—

TABLE XXII.—AVERAGE COMPOSITION OF CAROLINA PHOSPHATE.

	Per cent.
Phosphoric acid	25 to 28
Carbonic acid	5 ,, 11
Sulphuric acid	0·5 ,, 2
Lime	35 ,, 42
Magnesia	traces to 2
Ferric oxide	1 to 4
Fluorine	1 ,, 2
Sand and silica	4 ,, 12
Organic matter and combined water	2 ,, 6
Moisture	0·5 ,, 4

Florida.—This peninsula of the American continent contains, throughout its whole length, phosphatic deposits of great magnitude, but which were not utilized before 1890. Dr. Simmons of Hawthorn in 1879 discovered that the chief quarries of building-stone of Central Florida contained a considerable amount of phosphoric acid. Again, Francis Le Baron, a French engineer of Jacksonville (Fla.), discovered in 1884 the deposits of fossil bones forming the bars of Peace River, and also sent at the time several barrels to the Smithsonian Institution in Washington. This engineer returned to the district in 1886, made measurements and estimated the profits to be drawn from the working of these superficial deposits. When these were published, Col. T. S. Menchald installed in 1877 phosphate works to exploit the nodules, and sent his first delivery to the Scott Manufacturing Co. of Atlanta, Georgia. In June, 1889, Albert Vogt discovered the hard rock phosphate in sinking for water about twenty miles S.W. of Ocala, a small town in Central Florida. The Dunellon Phosphate Co. was then formed to buy and exploit several thousand acres on the alignment of the hard rock phosphate. Since that time the different kinds of phosphate as rocks, and as nodules, have been actively prospected for, and recognized over a tract 200 miles long by 6 miles in width. This belt is developed, parallel with the coast of Florida, at an average distance of 26 miles, and extends from the district of Richland, Pasco County, to the north as far as the environs of the River Apalachicola, bending towards the west and the south. The most important deposit of nodules (Land Pebbles) was discovered in 1890, in the neighbourhood of Bartow (Polk County). As far back as 1892, both rock phosphates and nodule phosphates were known with diverse percentage contents and values far beyond

the rivers Apalachicola in the west and north, and Caloosabatchee in the south. Throughout all these districts, representing a length of 400 miles, the exploitation has been followed up with feverish enterprise, and the quantities marketed, not only in the United States but in Europe, have rapidly increased. So as to be able to give some details of the nature of the phosphates collected in this region, the geology of Florida will not be discussed.

Description of the Deposits.—Four kinds of phosphates are differentiated by the following names, viz. Hard Rock, Soft Phosphate, Land Pebbles, River Pebbles.

Hard Rock.—Rock phosphate as a type is hard, compact, with a fine homogeneous grain, usually a pale yellow with irregular cavities often coated with mamillary concretions of phosphate of lime. These cavities are sometimes filled with amorphous phosphate of argillaceous aspect, due to the transport by water of particles of phosphate in suspension. The hard rock deposits of the Eocene are concentrated in a narrow belt of about 144 miles long, almost parallel with the West Coast of Florida, and at a distance from the sea varying between 25 to 50 miles. Taken as a whole, hard rock occurs as a conglomerate of boulders, cemented by a gangue, consisting of phosphatic sand, clay, or other detritus from the disintegration of the hard rock, and which constitutes the soft phosphate. The magnitude of these deposits of hard rock vary considerably. Near Dunellon they are often 40 to 50 feet thick, elsewhere only 5 to 10 feet. On certain points phosphate is found on the outcrops, especially in Levy County, but more often it is covered by a layer of sand 10 feet thick. There are two kinds of rock phosphate, solid rock and laminated rock. The solid rock is more or less homogeneous, of a white, grey, or yellow colour, sometimes deep blue or black, but more often it is marbled. The hard rock of good quality contains 77 to 82 per cent of phosphate of lime, and 3 per cent of oxides of iron and alumina. The analysis of a fine sample of hard rock gave the following figures :—

TABLE XXIII.—ANALYSIS OF A FINE SAMPLE OF HARD ROCK PHOSPHATE.

	Per cent.[1]
Water	0·92
Calcium fluoride	4·4
Phosphate of lime	83·14
Carbonate of lime	3·63
Oxide of alumina	1·52
Oxide of iron	8·45
Silica	4·13

The analysis of two cargoes of 800 tons each, from the Blue River Phosphate Co., gave :—

[1] Totals to 106·19 ; the error is evidently in the oxide of iron.—Tr.

TABLE XXIV.—ANALYSES OF HARD ROCK BLUE RIVER PHOSPHATE.

	I.	II.
	Per cent.	*Per cent.*
Water	0·52	2·80
Phosphate of lime	81·59	78·19
Oxides of iron and alumina	2·06	2·95

The laminated rock, the crevices of which are generally filled with clay, rarely sand, frequently contain 5 to 8 per cent of clay, from which it is partially freed by roasting, grinding, and sifting. It then only contains 3 to 4 per cent of oxides of iron and alumina, and is exported. The material passing through the sieve contains up to 10 per cent of clay, and is utilized in the country itself. This roasting of the phosphate is carried out in a very primitive manner: on a layer of wood 1 foot thick is placed a layer of phosphate 3 to 4 feet thick, and fire applied. This method is decidedly economical, but it yields a bad product. Whilst the phosphate of the lower layer is roasted, that on the top is barely dried, and the whole mixed with ashes and pieces of charcoal. But the roasting has little effect on the moisture content of the phosphate, for it suffices to expose it to the open air for it to recover 1 to 3 per cent of water.

Plate Rock or Sheet Rock.—This kind of phosphate is the most interesting of all. It is found near Ocala, especially near Anthony, Spar and Montagne. It occurs as small tablets, or as large as the hand, of irregular shape of one to several centimetres thick, of a white or brownish-yellow colour. The heavy, brittle fragments are the richest in phosphoric acid, whilst the soft, light fragments contain the most clay. The sorted pieces contain sometimes as much as 80 per cent of phosphate, and only 1 to 2 per cent of oxide of iron and alumina; the average is 74 to 78 per cent of phosphate of lime, with 3 to 4 per cent of oxide of iron and alumina. This high iron and alumina content comes from the gravel mixed with it, which forms irregular fragments of phosphate, the crevices of which are filled with clay. The plate rock rests always on the dolomitic limestone which forms columns and irregular cones. The cavities comprised between these columns are filled with phosphate, mixed with sand or clay. In certain places the phosphate bed is very pure and contains 50 to 80 per cent of pure phosphate. The superficial layer of sand is usually not very thick, but it is sometime 45 to 50 feet thick.

Soft Phosphate.—There is known under this name, in Florida, a phosphatic clay of soft, friable, or kneadable consistency, with a very variable moisture content, which constitutes the filling between the pebbles. As the following analyses show, a small portion of its phosphoric acid is sometimes soluble in water or in citrate :—

Soft Phosphate of Palk County.—Water 8·35 per cent; phosphoric acid, total 28·9 per cent, of which 0·87 per cent is soluble in citrate (Wagner's method) and 2·05 soluble in citrate (Petermann's method); 2·83 per cent of oxide of iron, and 0·86 per cent of clay.

Soft Phosphate of Alafia Creek.—Water 5·8 per cent; phosphoric acid, total 9·4 per cent, of which 0·62 per cent is soluble in water; oxide of iron 7·5 per cent; clay 10·26 per cent. This quality of phosphate is used directly as manure, being simply ground fine.

River Pebbles are found in several rivers of the west part of Florida, chiefly in Peace River and Alabama River, where they sometimes form considerable deposits. This phosphate can be extracted cheaper than all others. Powerful dredges fitted with centrifugal pumps lift the sand and pebbles; these are afterwards separated from the sand by a slightly inclined rotary sieve consisting of iron rods. The sand passes through the meshes, and returns with the water into the river, whilst the phosphate issues from the sieve at the lower extremity, mixed with stones and pieces of wood. It is taken to the dryer without further cleaning. The daily yield of a dredge varies according to the quality of the material lifted by the pump. Thus on certain points of the river the phosphate is very pure, whilst on others nothing but sand is found. Some days 100 tons of phosphate are collected, other days only 20 tons. The installations at work on Peace River produce on an average 50 tons of phosphate per day. The cost of extraction of river pebbles is in general not heavy; however, the cost price per ton exceeds a dollar on an average. The waters of Peace River incessantly bring phosphates to certain points, and remove it from others. Whatever may be the importance of the deposits of Peace River phosphates, they are not inexhaustible, and the time can be seen when they will cease to be workable. River pebbles are in the form of nodules, the size of which varies from sand grains to nuts. The corners are rounded, and the surface is often polished and brilliant. The colour is dark-grey, blue, or black. The land pebbles, from which the river pebbles are formed by washing, are generally pale, and it is believed that the black colour of the river pebbles comes from the tannin of the plants which grow on the banks of the rivers. Analysis reveals no difference between the two phosphates. Both have the same composition, 65 to 70 per cent of phosphate of lime, with less than 3 per cent of oxide of iron and alumina. However, the impurities found mixed with river pebbles have the effect of bringing the phosphates of lime down to from 60 to 65 per cent.

Land Pebbles.—All the country, between Peace River and Alafia River, in the counties of Polk, Hilsborough, de Soto, Manatee, contain phosphate deposits. The richest region is a strip of land

about 160 square miles, between Barlow, Fort Meade, Chicora, and Callsville. The land of this district is flat like all South Florida, with low undulations here and there. Under the surface bed of sand, phosphatic clay is found almost everywhere. As already mentioned, land pebbles can hardly be distinguished from river pebbles. They are paler and purer than the latter; their phosphate of lime content reaches 72 to 75 per cent, on an average 66 to 68 per cent, with 2·3 per cent of oxide of iron and alumina. An average sample gave the following results :—

TABLE XXV.—ANALYSIS OF LAND PEBBLE PHOSPHATE.

	Per cent.
Phosphoric acid	33·61
Loss on ignition	0·79
Lime	48·08
Oxide of iron	1·20
Oxide of alumina	1·38
Magnesia	5·54
Carbonic acid	2·29
Silica	7·15

Tennessee.—As far back as 1892, the presence of a very extensive phosphate level in the south of the central region of Tennessee, chiefly in Mount Pleasant County, in the districts of Maury and Perry, was discovered. The bed is found below the Devonian schists of Chattanooga. The phosphate occurs under two different forms; in the upper part, that is to say, immediately below the greyish-blue shales of Harpeth, phosphatic nodules are found, then comes a bed of black schists termed Chattanooga, and finally a uniform bed of about 1 metre in thickness of rock phosphate resting directly on limestone which ends the formation. Samples of this rock phosphate from the best-known parts gave the following average results (D. Levatt) :—

TABLE XXVI.—ANALYSIS OF TENNESSEE ROCK PHOSPHATE.

	Per cent.
Phosphoric acid	26·74 to 31·94
Oxide of iron	2·32 ,, 6·92
Insoluble matter	2·70 ,, 7·06
Lime	29·60 ,, 41·30
Sulphur	0·00 ,, 4·00
Carbonic acid, CO_2	0·00 ,, 1·50
Moisture	0·20 ,, 0·60

Remarks on the Actual Condition of the Phosphate Industry in America.—In the Southern States of the Union, there is a manifest tendency to concentrate businesses into the same hands. Thus for the hard rocks of Florida, there were 70 declarations of exploitation in 1902, 60 in 1903, 18 in 1904, 14 in 1905, and 16 in 1906. On the exploitations declared in 1906, 10 were at work,

3 idle, and 3 in preparation. The total amount of rock phosphate marketed in 1906 was 2,080,957 long tons, of a value of 8,597,437 dollars, against 1,947,190 long tons in 1905. The production of Florida alone reached 62·4 per cent of the total production of the United States. The exports of hard rock were 565,953 long tons in 1906, against 595,491 long tons in 1905; they however exceed those of previous years. The exports of land pebbles to America and foreign ports, reached 482,232 long tons, against 385,915 in 1905. River pebbles were not exported in the two last years. The South Carolina output has continually decreased since 1893. The production of Tennessee rose in 1906 to 528,888 long tons. Tennessee phosphate occurs in three varieties, which are the blue or black rock, the brown, and the white. The quantities marketed in 1906 consisted of 93 per cent brown, 6·5 of blue, and 0·3 per cent of white. In the west part of Putnam County, a new deposit of blue rock phosphate has been discovered. This contained on an average 65 to 75 per cent of tricalcic phosphate and only 5 per cent of oxides of iron and alumina. Amongst the other phosphate producing states, during the years 1901 to 1906, there may be mentioned North Carolina, Pennsylvania, Arkansas, and Idaho. But the production of these states was very low, except Idaho. North Carolina produced 45 long tons in 1903, Pennsylvania 100 long tons in 1904.

In Arkansas the production continually increases, though slowly. Idaho promises to become a big producer of phosphates. The bed, at a certain place, has a thickness of 85 feet; the main bed is 5 to 6 feet thick.

X. Africa.—*Tunis and Algeria.*—These two countries contain enormous deposits of phosphates. As far back as 1873, Thomas discovered the existence in the region south of the Tell, in the province of Algeria, of a Suessonian formation, rich in phosphate of lime. In 1886, the same geologist, after a scientific expedition, published his first researches on the phosphate beds of the Regency. He had, more especially, examined the deposits in the neighbourhood of Gafsa, in Tunis, showing their continuation through the South Algerian region. The phosphate of these regions is found at the bottom of the *Eocene* in contact with the *Cretaceous*, from which it is separated unconformably by black muddy clays of variable thickness saturated with chloride of sodium and gypsum, with the characters of silex. These phosphate beds consist of alternations of marl and nodules of phosphatic limestones, covered in the south of the Regency by a bed of shelly limestone, which gives place to a thick formation of nummulitic limestone as it ascends to the north. The phosphate beds become at the same time more sandy and glauconitic.

Marly Phosphate in Nodules.—The phosphate of lime occurs in

nodules, in the foliated and generally highly gypsiferous marls which alternate with limestone beds. Teeth and debris of saurians and fish are found therein. These marls are unctuous and greasy to the touch, and contain as much as 7 to 8 per cent of organic matter still badly examined, but which neither dissolves in carbon disulphide nor in benzine. These foliated marls often pass to a nodular structure. They contain irregular layers of phosphatic nodules which occur in various sizes and shapes, generally rounded or striated, covered with a shining brown crust of characteristic appearance. The large nodules which are met with in these conditions, and which have the appearance of enormous coprolites, are on the contrary very poor. The phosphate is entirely concentrated in the shining surface crust, the interior is limestone. The small nodules of identical appearance, on the other hand, have a content which may reach 70 per cent of tribasic. The phosphatic marls contain besides their phosphates, small interstratified crystals of gypsum, nodules of celestine, strontium sulphate, and alkaline salts.

Phosphatic Limestones.—These phosphates alternate with the nodular marl. They occur as a granular, rather friable rock, the colour of which varies from a yellowish-grey to a greenish-brown. The quality most appreciated crushes easily between the fingers, and its density does not exceed 2 for the rock *in situ*. This rock is formed by the agglomeration into a more or less calcareous cement by many fine grains of all shapes; some round, covered with a brown, brilliant crust, consist essentially of yellowish phosphate of lime, with an earthy fracture, or of fibrous appearance; the others, grass green, of scaly texture or in very small masses, of a scoriaceous or corroded appearance, recall, by their aspect, certain glauconites. There also occur very small grains of hyaline angular quartz, and chemical analysis always shows in this rock an appreciable amount of free or hydrated gelatinous silica; finally, it is also very rich in organic debris, such as coprolites, similar to those of the foliated marls, teeth and fish bones, or of saurians, more or less disintegrated. When the calcareous element predominates in this rock, it becomes greyish, and much resembles the grey chalk (calcareous tufa) of Ciply. These bands of phosphatic limestone are extensive, and occupy a very variable position in the different deposits, but very constant in each of them. Their thickness varies from only a few centimetres up to three metres and more, which they maintain without interruption over distances of 50 to 60 km. (western chain of Gafsa). The deposits may be divided into four main groups. 1. Those of the Tebessa district; 2. Those of the district of Setif; 3. Those of the Guelma district; 4. Those of the Ain-Beida district. They contain 24 to 30·5 per cent of phosphoric acid.

TABLE XXVII.—COMPLETE ANALYSIS OF AN ALGERIAN PHOSPHATE.

	Per cent.
Moisture	5·03
Loss on ignition (less 7·5 per cent CO_2)	9·26
Phosphoric acid	30·38
Calcium oxide	49·53
Sulphuric acid	2·01
Oxide of iron	0·32
Oxide of alumina	0·47
Magnesia	1·01
Potash	0·15
Insoluble, etc.	1·85
	100·01

TABLE XXVIII.—ANALYSES OF TWO SAMPLES OF DJEBEL GOURNIA PHOSPHATE IN THE NATURAL CONDITION.

	I. *Per cent.*	II. *Per cent.*
Moisture	6·64	8·18
Organic matter	1·24	0·52
Silica	6·80	5·96
Phosphoric acid	24·93	27·01
Equal to tribasic phosphate of lime	54·42	58·96
Carbonic acid	8·52	7·30
Equal to carbonate of lime	19·34	16·57
Total lime	46·12	45·40
Magnesia	0·11	0·08
Manganese	traces	traces
Fluor	4·0	4·10
Calcium chloride	8·22	8·43
Oxide of iron	0·98	0·86
Alumina	0·20	0·16
On the dry sample	—	—
Phosphate of lime	58·30	64·05

XI. Asia.—Phosphate of lime deposits have also been discovered in Egypt, but their percentage of phosphate of lime does not exceed 50 per cent.[1] It has also been found in Palestine, to the west of the Jordan, near to the route followed by the caravans going from Damascus in Arabia, and testing 80 per cent of phosphate of lime, with 1 per cent of iron and alumina, and testing 10 per cent of calcium fluoride. These deposits are not yet exploited commercially.

XII. Phosphates of Oceania.—There is found in certain isles and on the coast of the Pacific Ocean considerable deposits of phosphatic material. Like Peruvian guano, which will be dealt with in the sequel, they are of animal origin, but they differ essentially from Peruvian guano by the almost complete absence of nitrogen, which they have lost either by decomposition or under the influence of

[1] Needless to say, Egypt is in Africa.—Tr.

climatic conditions in which they are found in the deposits, or by being carried away in its train by rain water. All phospho guanos resemble each other in their composition. They consist mainly of phosphate of lime, the content of which varies between 65 and 80 per cent and about 12 per cent of water. They moreover contain from 1 to 13 per cent of carbonate of lime coming from the coral limestone which serves to them as substratum, and about 1 per cent of nitrogen yielded by the organic matters which imparts to them a colour varying from yellow to dark brown. Finally, small amounts of oxide of iron and alumina, calcium fluoride, and analogous bodies, the presence of which, as will be seen further on, is calculated to interfere with the dissolving of the phosphates.

Phospho Guanos were formerly the most highly esteemed raw material of the manufacture of superphosphates and the most easily preserved. Unfortunately, the greater part of the deposits are partially exhausted, and those which still exist are not wrought, owing to the fall in price and the scarcity of labour. Phospho guanos differ much from each other in their appearance, their form, and their colour. They are met with, most often, in a pulverulent state, mixed with lumps, easy to crush between the fingers. They sometimes consist of masses, amalgamated with coral debris, sometimes as crusts, or again in masses as hard as stone. The chief deposits of these phosphates are met with in a great number of small islands in the West Indies and the Pacific Ocean, and also in the Bay of Mejillones on the West Coast of South America. A rapid description indicating their characteristics will now be given.

I. *West India Islands.*—Redonda Isles, Sombrero, Navassa, Aruba, Curaçao, Los Roques, Alta Vela, Rata.

II. *Islands of the Pacific Ocean.*—Baker, Jarvis, Malden, Fanning, Starbuck, Howland, Phœnix, Sidney, Enderbury, Minerva, Aves, Lacépède, Flint, Browse (? Brown), Fluon, Chesterfield, Abrolhos, Mona, Cayman, Clipperton, Nauru, Angaur, and Makatea Isles, etc.

West India Islands.—1. *Redonda Phosphate.*—This phosphate, like that of Alta Vela, does not contain phosphate of lime, but hydrated phosphate of alumina and phosphate of iron. It is thus unfit for making superphosphate. It is yellow in colour, more or less dark with black points. Its composition is as follows:—

TABLE XXIX.—ANALYSES OF REDONDA PHOSPHATE.

	Voelcker. *Per cent.*	*Tate.* *Per cent.*
Water	24·20	21·50
Phosphoric acid	38·52	38·50
Oxide of iron and alumina	35·33	32·50
Insoluble	1·95	6·50

2. *Sombrero Phosphate.*—Two sorts are to be differentiated: one of oolitic structure and variegated in colour, which contains besides tribasic phosphate of lime, phosphate of magnesia, phosphate of iron, phosphate of alumina, silica, and alumina; the other has a more homogeneous structure, a white or yellowish colour, is rich in phosphoric acid and contains in addition carbonate and sulphate of lime. This deposit was known in 1814, but it was only in 1858 that it was begun to be worked, and since then there has been drawn from it during long years excellent phosphate of lime, containing 75 to 80 per cent of $Ca_3P_2O_8$, 10 per cent of carbonate of lime, and 2 per cent of oxides of iron and alumina. But for the quality of the product since it began to be extracted below the sea-level, Voelcker gives the following analysis:—

TABLE XXX.—ANALYSIS OF SOMBRERO PHOSPHATE. (VOELCKER.)

	Per cent.
Water	2·94
Phosphoric acid	35·52
Lime	47·99
Oxide of iron	3·70
Alumina	7·55
Magnesia	0·58
Sulphuric acid	0·36
Carbonic acid	0·96
Fluorine	0·43

3. *Navassa Phosphate.*—The isle of Navassa is of coral origin, with escarpments in some places, and beaten by the waves in others. Phosphate was worked here as far back as 1856, but it was soon seen that it was rich in oxides of iron and alumina, and was abandoned. It is mostly granular, or in the form of grains, the size of which varies from that of a pin-head to that of the fist, and which are often agglomerated into big lumps of almost pure phosphate of lime. Its composition is the following according to Bretschneider (I) and Gilbert (II):—

TABLE XXX. (A)—ANALYSES OF NAVASSA PHOSPHATE.

	I. *Per cent.*	II. *Per cent.*
Water	5·73	3·01
Combined water and organic matter	4·93	7·17
Phosphoric acid	31·69	33·28
Lime	38 00	40·19
Oxide of iron	4·25	11·67
Alumina	8·81	
Sulphuric acid and fluorine	1·10	—
Carbonic acid	2·40	2·15
Insoluble	3·09	2·53

4. *Aruba Phosphate.*—This phosphate occurs as yellowish stones traversed sometimes by dark-coloured veins and spots. It contains

about 30 per cent of phosphoric acid, and 6 per cent of oxide of iron and alumina.

5. *Alta Vela Phosphate.*—This phosphate has a composition analogous to that of Redonda phosphate, as the following analysis shows:—

TABLE XXXI.—ANALYSIS OF ALTA VELA PHOSPHATE.

	Per cent.
Phosphoric acid	37·00
Oxide of iron	24·00
Alumina	15·00
Lime	1·00
Sesquioxide of chromium	0·75

6. *Rata or Fernando Noronjo Phosphate.*—This phosphate occurs as a fine powder; it also is very rich in oxides of iron and alumina, and thus unfit for superphosphate manufacture. It contains about 26 per cent of phosphoric acid and up to 20 per cent of oxides of iron and alumina.

7. *Monk's Island (Caribbean Sea) Phospho Guano.*—This phosphate contains 42 per cent of phosphoric acid and only 40 per cent of lime. It consists therefore partially of monacid phosphate. Its analysis gave the following results:—

TABLE XXXII.—ANALYSIS OF MONK'S ISLAND PHOSPHATE.

	Per cent.
Nitrogenous organic matter and combined water	7·60
Sulphate of lime	8·32
Phosphate of lime and magnesia	70·00
Alkaline salts	1·88
Carbonate of lime	10·20
Carbonate of magnesia	
Insoluble silicious residue	2·00
	100·00

The surface of this deposit, which is as hard as a rock, has not the same composition as the centre. Thus the bed having been carefully analyzed yielded 70 per cent of phosphate of lime on the surface, 74 per cent in the centre, and 75 per cent in the lower part.

8. *Christmas Island Phospho Guano* (Indian Ocean).—Christmas Island, to the south of Java, belongs to the Straits Settlements. The phosphate deposit discovered there a few years ago is wrought by a British Company, The Christmas Island Phosphate Co. Ltd. The total bulk of this deposit is estimated at 250,000 tons, with a percentage of 60 to 90 of phosphate of lime. The samples received in Europe tested 85 per cent of phosphate of lime with 1·5 per cent of sesquioxides; rendered soluble by sulphuric acid at 53° B., yielded about 20 per cent of phosphoric, of which 0·5 per cent was insoluble in water, and 4 per cent of free acid, which is little. This phosphate is very hard, but easy to crush when it is

dry, or dried, which is indispensable, as it contains 5 per cent of moisture.

Pacific Ocean Isles.—There are a series of coral isles in the Pacific Ocean, in the neighbourhood of the equator, deprived of all vegetation, which have hardly attracted attention. A sample was brought in 1853 to America of a non-nitrogenous guano, collected in one of these islands, Baker Island. Soon afterwards it was found that the other isles of the same group were equally rich in guano, viz. Howland, Malden, Jarvis, Starbuck, Enderbury, and finally the Phœnix Isles, a little further west. As Baker Isle, now for the most part exhausted, yielded the best guano, the typical guano of the isles of the group, a short description of it is now given.

Baker Island Guano.—Baker Island is situated at 0·14 of north latitude and 176·22½ degrees of longitude west of Greenwich; 1750 metres (say 1 mile) long its width is 1100 metres, and its height above the level of the sea is about 8 metres (26 feet). The chain of coral rocks which surround it, is dry over a surface of 160 metres. On this chain is a height of stones, corals and shells, which surround the actual guano deposit.[1] The vegetation of the isle only comprises rare species. The bed of guano is 15 cm. (6 in.) thick on the shore, and 1·60 metres, say 5½ feet, in the centre. Its surface is plane, and it occupies a surface of 62·5 hectares, say 156¼ acres. The guano isles are the refuge of sea fowl, which come there to make their nests and sit on their eggs. Their excrements, the food which they bring there (fish and other marine animals), and finally their dead bodies give birth to guano which is, therefore, constantly in course of formation. Looking to its formation, this guano, like that of Peru, to be described further on, should be very rich in nitrogen, but it is not so. Although rain is generally a rare phenomenon in these tracts, yet the guano is constantly washed by the waves, which are continually broken against the coral chain which fringes the islands. To that has to be added the heat of the day, which is very intense. It follows that the nitrogenous matters are rapidly decomposed, producing ammonia and nitric acid; the first is carried away by the wind, the second is converted into nitrate of soda, which is lost in the depths of the ocean. All the Pacific guanos are met with as a fine pale or dark brown powder according to their percentage of moisture. The brown powder is mixed with larger white granules, consisting in great parts of phosphate of ammonia and magnesia.[2] According to an analysis of Liebig, Baker guano contains:—

[1] The Pacific Isles are all protected on the sides of the prevailing winds by a chain of coral against which the sea waves are broken up.

[2] It follows from researches made since, that the magnesium phosphate in the guano is not tribasic but monacid; only traces of carbonate of lime were found therein. The composition of the guano is slightly modified since it has

TABLE XXXIII.—ANALYSIS OF BAKER ISLAND GUANO.

	Per cent.
Tribasic phosphate of lime	78·79
Tribasic phosphate of magnesia	6·12
Iron phosphate	0·12
Sulphate of lime	0·13
Alkalies	0·85
Chlorine	0·13
Ammonia	0·07
Nitric acid	0·45
Water, sand, etc.	13·34
	100·00

Baker Island was the first island in the Pacific Ocean in which guano was discovered and exploited. It is not, therefore, astonishing that the deposit is partially exhausted.

Other isles in the Pacific Ocean contain vast quantities of phospho guano, absolutely similar in composition to that of Baker Island. But the greater part of these deposits are only of historical value seeing that, if they are not exhausted, their output is insufficient. Thus the deposits of Baker Island, Lacépède, Malton, and Pelsart, would appear to be far from exhausted, and still to contain enormous quantities of guano. But the greater number of the islands are abandoned, because the cost of working and freights are too high for the selling price of the guano, which at the present time cannot compete with mineral phosphate.

Jarvis Guano is a mixture of powder, hard plates, and somewhat friable stratified fragments. The plates have a porcelain character sometimes semi-milky, already found in analogous guanos. Perfectly dried in an oven at 100° C. (212° F.) these fragments preserve their appearance. By detaching the stalagmites, which cover the plates, it has been found that they owe their semi-transparent appearance to the hydration of the phosphate of lime, evidently precipitated in a very slow manner. The phosphate so hydrated cannot, in fact, lose its water, except at a red heat, and the hard Jarvis plates still contain 11 or 12 per cent, which analysts have often confounded with organic matter, when they have ignited the manure after simple drying in the oven. This physical state of the phosphate of lime may be understood by going back to the phenomena which have successively led to the evaporation of the nitrogenous substances in the guano. Such phenomena cause the partial solution of the phosphate of lime, then later on,

been wrought in an intensive manner. Some per cents of carbonate of lime are always found in it, and only 75 per cent of tribasic phosphate of lime. The above analysis may also apply to all analyses of this class, from the point where they do not contain large amounts of gypsum, sand, and analogous impurities, as certain guanos from Jarvis Island.

its slow precipitation by the ammonia liberated, hence the explanation of the stalagmites and the hydration so conducive to the solubility of the manure in the soil.

TABLE XXXIV.—ANALYSIS OF JARVIS GUANO.

	Per cent.
Phosphate of lime $3CaO,P_2O_5 = 17{\cdot}397$ / $2CaO,P_2O_5 = 16{\cdot}026$	33·423
Phosphate of magnesia	1·241
Phosphate of iron	0·160
Sulphate of lime	44·549
Sulphuric acid, potash, chlorine / Organic matter and water	20 880
	100·259

The following are some analyses of phospho guanos by Dr. H. Gilbert :—

TABLE XXXV.—ANALYSES OF FANNING ISLAND GUANO.

	Per cent.	*or*	*Per cent.*
Water	8·0	Water	8·00
Carbonic acid	1·30	Carbonate of lime	2·97
Sulphuric acid	0·19	Sulphate of lime	0·32
Phosphoric acid	34·16	Tribasic phosphate of lime	73·00
Lime	42·84	Tribasic phosphate of magnesia	1·33
Magnesia	0·61	Calcium fluoride	2·06
Fluorine	1·01	Organic matter	13·32
Organic matter	12·32		[1] 101·00
	100·43		
Deduct oxygen equal to the fluorine	0·43	[1] 100 in original.	
	100·00		

TABLE XXXVI.—ANALYSES OF BROWN ISLAND GUANO.

	Per cent.	*or*	*Per cent.*
Water	15·0	Water	15·00
Carbonic acid	1·48	Carbonate of lime	3·36
Sulphuric acid	1·01	Sulphate of lime	1·72
Phosphoric acid	31·40	Tribasic phosphate of lime	68·00
Lime	39·94	Tribasic phosphate of magnesia	0·46
Magnesia	0·21	Oxide of iron	0·32
Oxide of iron	0·32	Sodium chloride	0·14
Soda	0·06	Calcium fluoride	0·70
Chlorine	0·08	Organic matter	10·30
Fluorine	0·34		100·00
Organic matter	10·30		
	100·14		
Deduct oxygen equal to fluorine	0·14		
	100·00		

TABLE XXXVII.—ANALYSES OF LACÉPÈDE ISLAND GUANO.

	Per cent.	*or*	*Per cent.*
Water	12·40	Water	12·40
Carbonic acid	0·86	Carbonate of lime	1·95
Sulphuric acid	0·10	Sulphate of lime	0·17
Phosphoric acid	33·64	Tribasic phosphate of lime	71·04
Lime	40·80	Tribasic phosphate of magnesia	2·03
Magnesia	0·93	Oxide of iron	0·75
Oxide of iron	0·75	Sodium chloride	0·16
Sodium	0·06	Calcium fluoride	1·58
Chlorine	0·10	Organic matter	9·92
Fluorine	0·77		
Organic matter	9·92		
	100·33		100·00
Deduct O = F	0·33		
	100·00		

Mejillones Guano.—This guano, so appreciated formerly, is now only of historical interest. From the rocky coast, for a length of almost twenty-five miles, which Bolivia has conquered from Peru and Chili, there starts a promontory about ten miles long which juts into the sea for a length of three miles, under the tropic of Capricorn, the rocks of which form a shade to the Bay of Morena on the south, and to the Bay of Mejillones on the north. This latter bay, well-sheltered from wind and wave by the point of Leading Bluff Peninsula, forms an excellent harbour, into which the ships come to load guano. The country, moreover, is almost unhealthy. The complete absence of rain, the frequency of violent winds and dense fogs, which last for ten hours, followed by a torrid heat under a brazen sky, a rocky, sandy soil void of all vegetation, and above all, the want of potable water, renders a sojourn in these tracts exceedingly trying. The inhabitants of the capital—the number of which was formerly very small, and has not increased by the working of the guano—are revictualled by the Pacific steamers, which call there and possess coaling-stations. Water is got by distilling sea water. The rocky peninsula, of an average height of 350 to 400 metres, looks like a sandy plain, only its promontory which protects the bay is more elevated, for it rises to 100 metres (5640 feet) to the west of the town ; to the north of this hill is the culminating point of the promontory, called Morro de Mejillones, of a height of 866 metres (2730 ft.). On the slope of this mountain, on the bay side, is the guano deposit. It is reached by a long road from the town, winding round the mountain. The principal deposit is found about 560 metres (1836 feet) above sea-level on the flank of the mountain ; in several points it is 14 metres, say 46 feet thick. The published information on the extent of these

deposits differ considerably; official data speak of 3,000,000 to 4,000,000 tons, other information represent the situation under a less alluring aspect, and assert that the reserves are almost exhausted. A road has been built, with great difficulty, across the mountain to connect the deposit with the loading quay. At a mile from the works the road divides into two—the one at a very rapid incline leads to the harbour, whilst the other leads to a tent constructed on the edge of the plateau where the guano, which is lifted there in sacks, is run into a shoot of 233 metres deep, which diverts into a warehouse situated in the port. In the centre of the port dwell the workmen, the overseers, the exporters, and the state government employees. The latter weigh the guano, which is then conveyed in trucks on rails to the other extremity of the harbour, and discharged into ships. The formation of Mejillones guano is analogous to that of Baker guano. As the climate here also is very dry, the absence of nitrogen can only supervene from the possible contact of sea water. The volcanic nature of these countries being granted, the periodical upheavals and sinkings of the ground are known historical facts, and it is known that on these occasions violent high waves are frequent.

Mejillones Guano, like Baker guano, is a brown powder mixed with more or less large friable lumps, consisting in part of phosphate of ammonia and magnesia. In the early days, this guano was frequently mixed with granite chips, from the rocky bed on which the deposits lie. But afterwards the importers installed crushers and driers, which have enabled them to eliminate the stones and to dispatch the guano as a uniform powder. Amongst the numerous analyses published, that by Fresenius and Neubauer is reproduced here. These chemists found in the sample dried at 100 the following results:—

TABLE XXXVIII.—ANALYSIS OF MEJILLONES GUANO.

	Per cent.	
Tribasic phosphate of lime	60·564	with 38·404 total P_2O_5
Monacid ,, ,,	17·960	
Sulphate of lime	1·069	
Carbonic acid	2·052	
Phosphate of iron, etc.	0·072	
Water and organic matter	10·161	together 0·729 N
Ammonia oxide	0·018	
Sulphate of magnesia	1·528	
Nitrate of magnesia	0·034	
Common salt	3·739	

Dr. Gilbert gives the following analysis:—

TABLE XXXIX.—ANALYSIS OF MEJILLONES GUANO.

	Per cent.
Water	9·14
Carbonate of lime	0·32
Sulphate of lime	3·26
Phosphate of lime basic	33·64
Phosphate of lime monacid	26·44
Phosphate of magnesia monacid	10·35
Oxide of iron and alumina	1·35
Silica	0·89
Sodium chloride	7·32
Organic matter	7·29
	100·00

As will be seen from these analyses, about one-fourth of the phosphoric acid is combined with magnesia. And if the phosphate of magnesia is in itself more soluble than phosphate of lime, it is so to a still greater extent in the case of monacid phosphate of magnesia.[1]

Clipperton Island Guano.—The discovery of guano deposits in Clipperton Island is more recent. This island is situated in the open sea off the coast of Brazil. The coral chain surrounds a fresh-water lake in mid ocean and has served as a refuge to sea birds for thousands of years. Whilst the nitrogen of the excrement was carried away by rain water the phosphoric acid combined with the lime of the coral. The whole of the isle is covered with phosphate to a depth of six feet. The average analyses of thirteen samples taken in different sections, has given 83 to 86 per cent of tribasic phosphate and 0·03 of oxide of iron and alumina. In the dry state the phospho guano is a yellowish sandy powder. Dr. Gilbert gives the following analysis:—

TABLE XL.—ANALYSIS OF CLIPPERTON ISLAND GUANO.

	Per cent.
Water	3·80
Tribasic phosphate of lime	78·09
Phosphate of magnesia	0·55
Carbonate of lime	6·73
Quicklime	2·84
Sulphate of lime	0·78
Sodium chloride	0·15
SiO_4	0·28
Organic matter	4·83
Oxide of iron and alumina	0·04
Undetermined	1·91
	100·00

[1] The translator dissents; no superphosphate made from material containing organic matter to the extent to which phospho guano does, approaches a bone ash superphosphate in this respect. For whiteness free from a yellow

The points of the Chipana Coast, Pabellon de Pira, Punta de Lobos, Huanillos, the Ballestas Isles, Guânape, Macabi, Lobos de Afuera, etc., contain considerable deposits.

Nauru Guano.—Nauru Isle, attached to the German protectorate of the Marshall Isles, is in 0·26 of S. latitude and 166·55° of E. longitude. Whilst the atolls of the Pacific scarcely rise 3 metres (10 feet) above high water, the Isle of Nauru rises about 75 metres, with an area of 2000 hectares (5000 acres). A bank of coral chains 60 to 90 metres wide (195·6 to 295·2 feet) go right round the island. To that succeeds a flat zone 100 metres wide covered with coconut trees; behind rises a rocky region, which consists of a mass of phosphate of great richness. No one knows the depth of this deposit, but the beds known are so extensive that their working may last for several generations. The quality of this phosphate would appear to be superior to that of all the phosphates known up to now, both as regards the richness and regularity of the phosphoric acid content, 86 to 87 per cent $Ca_3P_2O_8$, as well as the small proportion of oxide of iron and alumina.

A good part of the exports of Nauru phosphate goes to countries washed by the waves of the Pacific, Japan, Australia, New Zealand, and Honolulu, but France, Belgium, Great Britain, Sweden, Norway, Russia, and especially Germany likewise import large quantities.

Angaur Island Phosphate.—The deposits of Angaur Island phosphate comprise about 2,500,000 tons which may be extracted in the open air. Four-fifths of the deposit consist of a phosphate with a content of 80 per cent of tribasic phosphate of lime. Working reserved for thirty-five years to a German company with a capital of 4,500,000 marks, say £225,000.

Makatea Isle Phosphatic Deposits.—There has been discovered in the island of Makatea deposits of phosphate containing according to the analyses made from 60 to 85 per cent and even 90 per cent of pure phosphate of lime. Makatea Island belongs to the Paumotou Archipelago, and lies 120 miles to the north of Tahiti. It is $4\frac{1}{2}$ miles long and $1\frac{1}{2}$ miles wide. Its formation differs from all the other islands of the Paumotou group, in that it has no lagoon, and rises up to 230 feet, whilst the other islands are simple chains of an average height of 8 feet above sea-level. Phosphate has been found in several of these atolls, especially in that of Niau. Guano has also been found in Puka-Puka in the extreme north-west of the group.

The deposits of Makatea are valued at 30,000,000 tons and will be exploited by a French company.

cast it is only excelled by apatite. As to Mejillones guano, with 7 per cent of organic matter, it yields a superphosphate the colour of peat—as it passes into lignite—and the farmer does not like such a colour even in a compound manure far less in a superphosphate. So dark is this colour that it can only be used sparingly even in compound manures where the raw materials are sent up the cups and not dry mixed.—Tr.

Distribution of Phosphates in the Different Geological Formations.—On examining the subject from a geological point of view, phosphoric acid, or phosphoric acid and nitrogen, is found in the following formations :—

I. *Gneiss Epoch*, as apatite in Sweden, in Finland, in Norway, in the mountains of the east coast of North and South America.

II. *Palæozoic (or Primary) Epoch.*—1. *Silurian Formation.*—As phosphorites in Spain and in the south of Russia. 2. *Devonian Formation.*—As phosphorites in Germany. 3. *Carboniferous Formation.*—As Blackband in Great Britain and Germany.

III. *Mesozoic or Secondary Epoch.*—1. *Trias Formation.*—As Bone Bed and fossil bones in England, Germany, and Switzerland. 2. *Jurassic Formation.*—As coprolites in Germany and England. (*Lias.*)—As phosphatic nodules in France and Germany. (*Osteolithes.*)—As phosphorite in French Jurassic marls. 3. *Cretaceous Formation.*—As coprolites in France, in England, in Germany, and in Holland. As phosphorite in Spain, in Belgium, in France, in Austria-Hungary and in Russia.

Cainozoic or Tertiary Epoch.—Eocene Formation.—As coprolites in England and Germany. As phosphates in France, Algeria, Tunis, the Carolinas, Tennessee and Florida.

Quaternary and Recent Epoch.—1. As *fossil bones.*

2. As phosphate in the islands of Navassa, Redonda, Rata, St. Martin, Curaçao, Testigos, Buenos Aires.

3. As guano crusts in the islands of Starbuck, Flint, Sombrero, Avalo, Los Roques. As phospho guano in the islands of Baker, Howland, Fanning, Jarvis, Malden, Mary, Enderbury, Phœnix, Sydney, Vivorilla, Mona, George, Raza, Clipperton, Monk's at Mejillones, in the islands of Leysan, French, Frigatte Shoal, at Bramble Cays, Shoal Bay, Shark's Bay, in the islands of Timor, Ashmore, Brown, Jones, Lacépède, Abrolhos, Huon, Birds, Kurian Murian, Swan, and at Algoa Bay.

4. As guano in Peru, Chili, Patagonia. In the islands of Galapagos, Bat, Ishaboe, Damaraland, and Saldanha Bay.

5. Bat guano on the Mediterranean coasts, Egypt, Sardinia, Galicia, Porto Rico.

It will be convenient to add to this classification, the substances, manufactured by industry, such as bone black (spent char), bone ash, artificial guano manufactured from the excrements and the dead bodies of animals; fishes, lobsters; in addition to the precipitated phosphate of glue and gelatine factories, and finally the phosphates of basic slag. The following table prepared by Dr. M. Ullmann contains the analyses of all phosphates known up to the present time. As this document is absolutely unique in scientific literature it is given here at the risk even of repeating what has been said previously.

Geographical Distribution of Phosphate of Lime and

Localities.	Longitude of Greenwich.	Latitude.	Designation.	Analysis.		
				Water.	Loss on Ignition.	Lime.
A. Europe.						
1. *Sweden and Norway.*	Degrees.	Degrees.		Per Cent.	Per Cent.	Per Cent.
Krageroe	11 E.	59 N.	Apatite	0·45	—	45·58
Langesund	9·7 E.	59 N.	Chlorapatite	0·32	—	51·02
2. *Germany.*						
Hartz	11 E.	52 N.	Apatite	1-2	—	—
Helmstedt	11 E.	52 N.	Phosphorite	4·2	—	—
Wasserleben	11 E.	52 N.	,,	6	—	—
Lahn et Dill	8 E.	50·5 N.	,,	3·85	—	37·31
Peine	10·2 E.	52·3 N.	Coprolites	—	—	—
Horde	7·5 E.	51·5 N.	Phosphorite	—	—	—
Amberg	12 E.	49·5 N.	Osteolite	—	—	—
Delme (Lorraine)	6 E.	49 N.		—	—	—
3. *Austria-Hungary.*						
Schlaggenwald(Bohemia)	13 E.	50 N.	Apatite	—	—	—
Lavanthal (Carinthia)	15 E.	47 N.	Phosphorite	—	—	—
Starkenbach (Bohemia)	15·5 E.	50·5 N.	Coprolites	—	74·03	12·26
Cracow (Galicia)	20 E.	50 N.	Bat guano	7·50	75·20	—
4. *Belgium.*						
Liége	5·5 E.	50·6 N.	Phosphatic chalk	0·93	2·83	40·64
Ciply	4 E.	50·5 N.	,,	1·52	—	45·45
5. *France.*						
Bellegarde-sur-Rhône	4·5 E.	43·7 N.	Coprolites	4·70	0·2	32·50
Somme	2 E.	50 N.	Phosphorite	1·69	—	47·34
Lot	1·5 E.	44·5 N.	,,	4·27	—	50·10
Vaucluse	5 E.	44 N.	,,	2·45	—	26·57
Ardennes	4·6 E.	50 N.	,,	—	—	—
Boulogne	1·5 E.	50·7 N.	Coprolites	0·84	3·14	33·06
6. *Italy.*						
Sardinia (Cagliari)	9 E.	39 N.	Bat guano	18·77	61·14	5·17
7. *Spain.*						
Caceres	6·5 E.	39·5 N.	Phosphate	0·721	—	—
Estremadura	6 W.	40 N.	Phosphorite	0·30	—	43·41

Guano Deposits and their Chemical Composition.

Analysis.									
Lime not combined with P_2O_5.	Oxide of Iron.	Alumina.	Magnesia.	Phosphoric Acid.	Nitrogen.	Tribasic Phosphate of Lime.	Carbonate of Lime.	Calcium Fluoride.	Name of Chemist who made the Analysis.
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
—	1·00	0·77	—	34·30	—	74·87	—	—	A. Retter
—	0·90	—	0·80	38·02	—	82·99	—	—	E. Güssefeld
—	2·4		—	18·32	—	35·45	7·10	—	
—	2·86	—	—	19·27	—	41·48	8·9	—	
—	1·72	—	—	18·18	—	39·70	7·9	—	E. Schulte
—	4·75	3·08	0·18	29·19	—	63·72	—	4·88 fluorine	Dietrich & König
—	Very rich in iron		—	34·35	—	abt. 75	—	—	
—	Up to 19 % of iron		—	19·5-21	—	44·20	—	—	
—	—	—	—	36·64	—	80	—	3·0	
—	Phosphate of iron & alumina 13-20 %		—	18·04	—	33·44	—	—	
—	—	—	—	30·59	—	66·79	8·54	5·26	Meusel
—	—	—	—	29·30	—	64·39	13·5	—	
—	—	—	1·31	6·99	—	15·25	—	—	Reuss
—	—	—	—	3·82	9·17	8·33	—	—	Scheibler
—	2·39		0·79	27·25	—	59·49	7·04	—	Anglo-Cont. G. W.
19·18	1·75	1·11	—	22·17	—	48·44	—	—	A. Grimm
—	16·90	—	—	12·12	—	26·40	—	—	Dugléré
9·17	2·21		0·78	32·25	—	70·42	9·10	—	A. Grimm
—	2·96		0·26	37·07	—	80·92	3·43	—	Ulex
—	3·30		0·53	19·90	—	43·44	0·84	—	E. Güssefeld
—	4·6	2·3	—	18·04	—	36·43	10-13	3·0	Delattre
—	2·89	3·09	0·58	21·06	—	45·97	—	—	
—	trace	trace	0·86	5·02	5·72	10·95	—	—	Pavesi & Rotond
—	0·91	0·427	—	29·455	—	59·594	13·227	0·983	
4·85	1·64		—	32·60	—	71·16	—	2·57 fluorine	Niederstedt A. Grimm

Geographical Distribution of Phosphate of Lime and

Localities.	Longitude of Greenwich.	Latitude.	Designation.	Analysis.		
				Water.	Loss on Ignition.	Lime.
	Degrees.	Degrees.		Per Cent.	Per Cent.	Per Cent.
Logrosan	5·5 W.	39·4 N.	Phosphorite	2·40	—	—
Truxillo	6 W.	39·5 N.	,,	—	—	—
8. *Russia.*						
Podolia	27·5 E.	48·5 N.	Phosphorite in balls	—	—	—
Kursk	36 E.	52 N.	Phosphorite	3·57	—	—
Woronesch	39 E.	52 N.	,,	—	—	—
9. *Great Britain.*						
Ipswich (Suffolk)	1 E.	52 N.	Coprolites	—	—	—
Cambridge	0 E.	52 N.	,,	4·01	—	45·39
Bedford	1·5 E.	52 N.	,,	—	—	—
Wales	4 W.	52 N.	,,	1·4	—	23·49
Lyme Regis	3 W.	50·7 N.	,,	6		—
Goodrich	2·5 W.	52 N.	Mineral phosphate	—	—	42·84
B. North America.						
10. *Canada.*						
Ontario	80 W.	45 N.	Apatite	0·08	—	—
Ottawa	75 W.	45 N.	,,	—	—	—
11. *United States.*						
New York	75·5 W.	44·4 N.	Apatite Laurenzia	0 2	—	51·48
South Carolina	80 W.	33 N.	Phosphate	1·56	—	42·28
Charleston	80 W.	33 N.	,,	9·95	6·65	31·12
Port Royal	81 W.	32·5 N.	,,	0·58	1·01	37·79
Tennessee	86 W.	35 N.	,,	0·80	—	50·60
Florida	80 W.	25·30 N.	,,	0·55	—	50·46
Tallahasee	84·4 W.	30·5 N.	,, (Hard rock)	0·25	—	—
Barlow	82 W.	28 N.	,, (Land pebbles)	—	—	—
Peace River	82 W.	27·5 N.	,, (River pebbles)	1·05	—	—
C. West Indies and Mexico.						
12. *West Indies.*						
Havana	82 5 W.	23 N.	Phosphate	11 90	—	—
Guanahani	74·3 W.	24 N.	Phospho guano	9·83	—	30·60
Vivorilla (Isle)	—	—	,,	7·0	6·46	45·26
Puerto Rico (Ponce)	67 W.	18 N.	Bat guano	17·68	51·66	10·17

Guano Deposits and their Chemical Composition—continued.

Analysis.					Nitrogen.	Tribasic Phosphate of Lime.	Carbonate of Lime.	Calcium Fluoride.	Name of Chemist who made the Analysis.
Lime not combined with P_2O_5.	Oxide of Iron.	Alumina.	Magnesia.	Phosphoric Acid.					
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
—	2·22		—	38·95	—	85·03	10·35	—	De Luma
—	little	—	—	35·50	—	75·80	little	14·0	
—	—	—	—	34·0	—	74·23	6·92	—	
—	1·95	—	—	35·42	—	77·34	—	—	Schwackhöfer
—	—	—	—	13·74	—	30·0	24	—	Pieper
—	5·0	4·0	—	24·73	—	54·0	10·0	3 fluorine	Völcker
—	1·87	2·57	0·48	26·75	—	57·12	—		,,
—	—	—	—	18·32	—	about 40	—	—	
—	7·47	5·70	—	15·4	—	33·62	—	—	Herapath
—	1·00	—	—	27·95	—	6·1	24 0	—	
—	2·36		—	27·63	—	60·32	9·54	—	
—	—	—	—	39·98	—	86·61	4·47	7·22	W. R. Hutton
—	0·09	0·57	0·15	39·0	—	85·24	0·06	6·8	
—	1·07		—	37·0	—	79·59	2·32	6·42	H. Gilbert
—	—	—	—	26·89	—	58·70	—	—	Völcker
—	2·86	2·38	1·62	20·92	—	45·66	—	5·11 of fluor.	Ulex
—	2·82	1·12	0·5	23·67	—	51·67	9·18	—	
7·20	3·32		—	36·69	—	80·09	—	—	H. Grimm
9·12	1·95		—	35·80	—	78·15	—	—	,,
—	0·82	1·27	—	35·42	—	77·32	—	—	Pieper
—	0·80	1·37	—	31·59	—	68·96	—	—	Völcker
—	0·52	1·64	—	28·08	—	61·30	—	—	Gilbert
—	2·88	—	—	34·08	—	74·40	—	—	Pieper
16·98	5·77		—	11·60	0·73	25·32	—	—	A. Grimm
—	0·25		1·27	32·24	0·13	70·38	—	—	H. Gilbert
—	1·59		0·17	7·57	8·35	16·52	—	—	A. Grimm

Geographical Distribution of Phosphate of Lime and

Localities.	Longitude of Greenwich.	Latitude.	Designation.	Analysis.		
				Water.	Loss on Ignition.	Lime.
13. *Lesser Antilles.* (*a*) Windward (Isles).	Degrees.	Degrees.		Per Cent.	Per Cent.	Per Cent.
Avalo (Isle) . . .	81 W.	22 N.	Guano in crusts .	20·12	—	31·15
Navassa (Isle) . .	75 W.	18·2 N.	Coralline phosphate	2·7	—	37·6
Mona (Isle) . . .	67·5 W.	18·1 N.	Phospho guano .	7·66	—	—
Sombrero (Isle) . .	63·5 W.	19 N.	Guano in crusts .	9·06	—	36·17
St. Martin (Isle) . .	63 W.	18 N.	Mineral phosphate	5·04	—	47·69
Redonda (Isle) . .	62 W.	17 N.	Phosphate of alumina	23·23	—	—
Alta Vela . . .	71·5 W.	17·5 N.	,,	16·49	—	—
14. *Lower Antilles.* (*b*) Leeward (Isles).						
Aruba (Isle) . . .	70 W.	12·5 N.	Mineral phosphate .	3·46	—	48·72
,, . . .	—	—	,,	2·16	—	47·84
Curaçao (Isle) . .	69 W.	12 N.	,,	0·84	—	51·00
Buenos Aires (Isle) .	68 W.	12 N.	,,	20·0	—	—
Los Aves (Isle) . .	67 W.	12 N.	Phospho guano .	5·93	—	37·92
,, . .	—	—	,, .	10·35	—	—
,, . .	—	—	,, .	14·90	—	—
Los Roques (Isle) . .	66·5 W.	12 N.	Guano in crusts .	10·22	10·22	38·67
,, . .	—	—	Phosphate of iron .	—	—	—
Testigos Isle . . .	63 W.	12 N.	,, .	12·17	12·17	0·37
15. *Mexico.*						
George (Isle) . . .	113 W.	31 N.	Phospho guano .	—	—	—
Raza (Isle of) . .	113 W.	29 N.	,, .	4·08	—	35·28
Clipperton (Isle) . .	108 W.	9 N.	,, .	3·80	4·83	49·25
D. South America.						
16. *Venezeula.*						
Maracaibo (Monkey Island) . . .	71 W.	12 N.	Phospho guano .	2·39	—	39·48
17. *Brazil.*						
Fernando Naronha (Isle of Rata) . . .	33 W.	4 S.	Phosphate . .	10·0	—	30·6
18. *Patagonia.*						
East Coast . . .	67·5 W.	49 S.	Guano . . .	16·15	28·06	20·20
Falkland (Isle) . .	60·0 W.	52 S.	,, . . .	8·86	17·10	—

Guano Deposits and their Chemical Composition—continued.

Analysis.					Nitrogen.	Tribasic Phosphate of Lime.	Carbonate of Lime.	Calcium Fluoride.	Name of Chemist who made the Analysis.
Lime not combined with P_2O_5.	Oxide of Iron.	Alumina.	Magnesia.	Phosphoric Acid.					
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
—	5·88	trace	0·44	24·36	0·45	53·18	—	—	A. Schlimper
—	14·8		0·6	33·5	0·11	73·13	5·6	—	Ulbricht
—	0·75		—	27·85	0·25	60·79	3·80	—	Weiss
—	2·42	6·89	0·36	34·41	—	74·55	—	—	Völcker
—	1·21	2·99	0·38	24·14	—	52·70	32·27	—	,,
—	36·38		—	36·95	—	80·66	—	—	,,
11·25	19·24		—	20·45	—	44·64	—	—	,,
—	3·25		—	36·29	—	79·22	—	—	E. Güssefeld
—	1·36	0·61	trace	33·82	—	71·65	10·66	—	A. Retter
—	0·2	—	0·97	39·96	—	87·23	6·99	0·48 fluorine	E. Güssefeld
—	—	—	—	21·76	—	45·50	—	—	,,
6·79	1·02		—	26·32	0·36	57·45	—	—	A. Grimm
—	0·164	—	—	29·02	—	63·37	12·83	—	
—	0·35		—	22·40	—	48·90	7·05	—	
—	0·40	—	2·75	40·49	—	60·80	—	—	Taylor
—	40·5		—	37·0	—	80·77	1·0	—	Schucht
—	13·30	—	0·57	17·41	—	38·0	—	—	Ure & Teschenmacher
—	1·50	—	—	37·71	—	82·33	—	—	E. Güssefeld
—	1·14	—	1·18	39·70	0·40	86·66	—	—	Fr. Voigt
—	0·04		0·25	36·07	0·06	78·84	6·72	—	H. Gilbert
—	—	—	1·17	41·34	0·139	90·24	—	—	Völcker
—	9·56	11	—	26·5	—	—	—	—	Schucht
1·95	0·99		—	15·43	4·40	33·68	—	—	A. Grimm
—	—	—	—	9·75	1·24	21·29	14·02	—	Anderson

Geographical Distribution of Phosphate of Lime and

Localities.	Longitude of Greenwich.	Latitude.	Designation.	Analysis.		
				Water.	Loss on Ignition.	Lime.
19. *Peru.*	Degrees.	Degrees.		Per Cent.	Per Cent.	Per Cent.
Lobos de Tierra (Isle) .	82 W.	6·5 S.	Guano . . .	23·79	—	18·91
Lobos de Afuera (Isle) .	81 W.	7 S.	,, . . .	19·60	—	—
Macabi ,, (Isle) .	81 W.	7·5 S	,, . . .	30·33	—	—
Guanape ,, (Isle) .	79 W.	8·5 S.	,, . . .	25·88	—	—
Chinchas (Isle) . .	77 W.	13·5 S.	,, . . .	—	—	10·99
Ballestas (Isle) . .	76·5 W	13·5 S.	,, . . .	14·87	—	—
Independencia Bay .	76 W.	14 S.	,, . . .	13·22	—	12·59
20. *Chili.*						
Pabellon de Pica . .	70 W.	21 S.	Guano . . .	13 05	—	14·23
Punta de Lobos . .	70 W.	21 S.	,, . . .	14·12	—	—
Huanillos . . .	70 W.	21·5 S.	,, . . .	14·12	—	—
Mejillones . . .	71 W.	23 S.	Phospho guano .	4·44	—	37·64
Angamos . . .	71 W.	23 S.	Guano . . .	7·39	64·81	5·11
Corcovado . . .	73 W.	43 N.	,, . . .	18·19	—	13·67
E. Pacific Ocean.						
21. *Sporadic Isles.*						
Fanning (Isle) . .	159 W.	4 S.	Phospho guano .	8·00	12·32	42·84
Jarvis (Isle) . . .	159·5 W.	0·5 S.	,, .	12·118	5·992	34·83
Malden (Isle) . .	155 W.	4 S.	,, .	4·78	5·18	46·229
Starbuck (Isle) . .	156 W.	5·5 S.	Guano in crusts .	10·01		44·96
22. *Phœnix Group of Isles.*						
Mary (Isle) . . .	171·6 W.	2·75 S.	Phospho guano .	5·63	—	44·40
Enderbury (Isle) . .	171 W.	3 S.	,, .	8·76	8·81	40·76
Phœnix (Isle) . .	170·45 W.	3·5 S.	,, .	4·93	8·66	44·91
Sidney (Isle) . . .	171·50 W.	4·5 S	,, .	7·38	7·59	42 96
23. *Gilbert Group of Isles.*						
Ocean (Isle) . . .	169 E.	1·5 S.	Phosphate . .	1·01	2·7	49·5
24. *Baker Isles* .	176·25 W.	0·13 S.	Phospho guano .	3·945	7·758	43·379
Howland (Isle) . .	177 W.	0·5 S.	,, .	5·34	—	44·48
F. Australia and Australian Isles.						
25. *Australian Continent.*						
Shark's Bay . . .	114 E.	26 S.	Phospho guano .	15	—	—

Guano Deposits and their Chemical Composition—continued.

Analysis.					Nitrogen.	Tribasic Phosphate of Lime.	Carbonate of Lime.	Calcium Fluoride.	Name of Chemist who made the Analysis.
Lime not combined with P_2O_5.	Oxide of Iron.	Alumina.	Magnesia.	Phosphoric Acid.					
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
—	1·89		0·27	17·54	5·58	—	—	These Guanos contain 2-5 % Potash.	Anglo-Cont. G. W.
—	—	—	—	16·70	3·60	—	—		
—	—	—	—	11·95	11·05	—	—		Ohlendorff & Co.*
—	—	—	—	12·25	11·0	—	—		,,
—	0·30	—	1·19	13·52	14·39	—	—		,,
—	—	—	—	12·23	12·50	—	—		,,
—	1·52		0·39	10·89	7·68	—	—		Anglo-Cont. G. W.*
—	2·73		0·20	12·78	8·88	—	—		,,
—	—	—	—	15·10	5·70	—	—		,,
—	—	—	—	13·30	6·60	—	—		
0·12	0·66	0·90	2·90	31·72	0·59	69·24	—	—	A. Grimm
—	0·88		1·11	7·13	19·28	—	—	—	Anderson
—	0·20		1·17	15·14	10·52	—	—	—	Anglo-Cont. G. W.
—	—	—	0·61	34·16	—	74·57	—	1·01 fluor.	H. Gilbert
—	0·09	—	0·568	17·67	0·647	38·57	—	—	V. Liebig
—	—	—	—	34·75	—	75·86	8·29	—	Völcker
—	—	—	—	40·12	—	87·58	—	—	,,
9·89	0·23		—	29·26	0·54	63·87	—	—	A. Grimm
—	—	—	—	28·74	0·38	62·74	16·50	—	Völcker
—	0·23		—	36·10	0·63	70·80	4·54	—	
—	0	0	2·03	34·41	0·28	75·13	6·0	0·82	H. Gilbert
3·19	0·42		—	38·73	—	84·65	4·91	1·0	V. Grueber
—	0·067	—	2·207	40·329	1·35	88·03	—	—	V. Liebig
2·29	0·18		—	29·75	0·53	64·94	—	—	A. Grimm
—	—	—	—	23·59	—	50-53	4·6	—	

* Same firm.—Tr.

Geographical Distribution of Phosphate of Lime and

Localities.	Longitude of Greenwich.	Latitude.	Designation.	Analysis.		
				Water.	Loss on Ignition.	Lime.
26. *Australian Isles.*	Degrees.	Degrees.		Per Cent.	Per Cent.	Per Cent.
Brown (Isle) . . .	123·5 E.	14 S.	Phospho guano .	15·00	10·30	39·94
Jones (Isle) . . .	126 E.	13 S.	,, .	7·93	10·92	42·86
Lacepedes (Isle) . .	122 E.	17 S.	,, .	6·78	10 54	41·33
Abrolhos (Isle) . .	113 E.	28 S.	,, .	4·48	—	43·20
,, . .	—	—	,, .	10·10	6·20	—
Huon (Isle) . . .	163 E.	18 S.	,, .	9·74	19·90	37·60
Bird's (Isle) . . .	156 E.	22 S.	,, .	10·70	9·70	—
Bat (Isle) . . .	146 E.	3 S.	Guano . . .	14·53	—	14·64
G. Asia.						
27. *Palestine.*						
Country East of Jordan	35·5 E.	32 N.	Phosphorite . .	—	—	—
28. *Arabia.*						
Kurian Murian (Isle) .	56 E.	17·5 N.	Phospho guano .	8·70	9·30	—
29. *Malay Archipelago.*						
Timor (Isle) . . .	124-127 E.	8-10 S.	Phospho guano .	6·25	—	40·33
Christmas (Isle) . .	105·5 E.	10·5 S.	Phosphate . .	3·05	—	—
H. Africa.						
30. *North Africa.*						
Algeria	3 E.	37 N.	Mineral phosphate	2·39	—	50·10
Tebessa	8 E.	35·5 N.	,,	1·97	—	50·30
Toqueville . . .	8 E.	36 N.	,,	0·77	—	—
Tunis	10 E.	37 N.	,,	5·95		45·35
Sfax	10·5 E.	34·5 N.	,,	—	—	—
Gafsa	9 E.	45·4 N.	Phosphate . .	2·6	2·99	45·12
Egypt	29 E.	31 N.	Bat guano . .	17·19	29·50	—
31. *South Africa.*						
Damaraland . . .	14 E.	22 S.	Guano . . .	18·89	—	12·42
Ichaboe (Isle) . .	15 E.	26·5 S.	,, . . .	17·97	17·0	—
Saldanha Bay . .	18 E.	33 S.	,, . . .	17·04	—	24·26
Algoa Bay . . .	26 E.	34 S.	Phospho guano .	20·25	12·10	—

Guano Deposits and their Chemical Composition—continued.

Analysis.					Nitrogen.	Tribasic Phosphate of Lime.	Carbonate of Lime.	Calcium Fluoride.	Name of Chemist who made the Analysis.
Lime not combined with P_2O_5.	Oxide of Lime.	Alumina.	Magnesia.	Phosphoric Acid.					
Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	
—	0·32	—	0·21	31·40	—	68·54	—	0·34 fluorine	H. Gilbert
2·38	0·33	0·54	—	34·22	—	74·70	4·25	—	A. Grimm
—	1·61	—	0·55	35·22	—	76·88	—	traces	Cherson
5·56	3·10		—	—	0·38	69·46	—	—	A. Grimm
—	1·67		0·97	33·67	—	70·32	—	2·57	H. Gilbert
—	0·24	—	0·09	28·59	1·16	62·41	—	traces	Chevron
—	—	—	—	—	1·24	23·15	36·45	—	Anderson
—	0·40	0·57	—	7·30	7·54	15·94	6·97	—	Völcker
—	0·64	0·48	traces	38·24	—	83·68	—	9·8	Elschner
—	—	—	—	26·24	1·37	57·30	—	—	Huson
3·49	1·48		—	31·14	0·82	67·98	6·23	—	A. Grimm
—	0·71	1·22	0·26	39·18	—	83·53	4·82	3·44	H. Gilbert
14·09	0·53		—	30·44	—	66·45	—	—	A. Grimm
—	0·55		0·50	28·16	—	61·47	20·19	—	A. Retter
—	0·98		0·81	26·32	—	57·46	22·80	—	,,
—	0·81	0·62	0·6	27·25	—	59·48	11·52	—	Schucht
—	1·2	0·6	—	27·2	—	59·0	14·0	—	?
—	1·68		0·5	27·23	—	59·44	11·95	—	Schucht
2·76	—	—	—	—	11·81	—	—	—	Völcker
—	—	—	—	13·40	8·88	29·25	—	—	A. Grimm
—	—	—	—	11·19	—	24·44	—	—	Anderson
—	2·27		0·97	24·52	1·41	55·40	—	—	H. Gilbert
—	—	—	—	6·68	0·43	14·60	—	—	Grouven

CHAPTER III.

DRYING AND ENRICHMENT OF PHOSPHATES.

Drying.—Phosphates, for all uses to which they may be put, must be dried and finely ground. When the phosphates are massive (rock phosphate) or in lumps, they may be completely dried in summer by storage in a warehouse with vents in the side; in winter, drying is finished in a drying machine. Formerly phosphates were calcined to increase the percentage of phosphoric acid and facilitate grinding (p. 85 *et seq.*). Drying is indispensable in the case of the sandy phosphates of Mons, Somme, and Cambresis. This operation is conducted in a naked fire drier, on cast-iron plates, about two-fifths of an inch thick, in contact with the flames of one or more furnaces, but protected from over-heating. The phosphate is spread on the drier, in layers of 4 to $5\frac{3}{4}$ inches thick, according to the nature of the phosphate. The drying reduces this thickness about one-third. An operation is finished in 6 hours over the flues above the flames; in 8 hours on the flues, forming the first circuit of the flames; and in 10 to 12 hours on the flues, forming the second and the third circuit. A drier of 250 square metres (820 square feet) may yield 35 to 40 tons of dry phosphate per day of 24 hours. The consumption of coal is about 2 cwt. per ton of sand obtained. The sands, so dried, pass into cylindrical sifting machines, with polygonal section like those of an ordinary mill covered with wire gauze Nos. 70, 80, 90, 100, 110, and fitted with baskets inside, in which to collect the larger fragments. The dry sand passes successively through the different mesh sieves, commencing with the larger sizes. The exit of the products is thus regulated in a uniform manner over the whole length of the apparatus. The residues on the sieves are crushed in flat stone mills revolving at a speed of 100 turns a minute. Each pair of stones absorbs 6 to 7 H.P. The sifted phosphate is generally 7 to 8 per cent richer in tribasic phosphate than the ground phosphate: the whole is mixed so as only to have one average quality of the appearance of finely ground pepper. When the phosphate is in nodules, as in Auxois, they must be crushed or cracked before grinding. The crushers and cracking machines, used in the Meuse and Ardennes, consist of two cast-iron cylinders, studded with

projecting teeth in the form of pyramidal trunks, which mutually intersect each other. At other times the crusher consists of a grooved mobile blade which crushes the phosphate against a fixed plate (see Fig. 12 and context). Where the nodules to be crushed are not quite dry, the working of the mills produces steam, which finds vent through wooden pipes fitted either to the boxes which collect the ground phosphate, or to the mill covers. These pipes, acting as evaporators, end on the roof. The steam carries with it entrained phosphate dust. Of late mechanical driers have been installed for drying raw phosphates.

Calcining the Nodules.—Before crushing the nodules, they were at first only dried in the sun, or on iron plates heated artificially. Lately they are calcined in special furnaces to free them completely from water and carbonic acid; their weight per cubic metre is thus lowered from 1000 kg. to 950 kg, say from 20 cwt. to 19 cwt., and the percentage of phosphoric acid is increased *pro rata*. These furnaces are 4·5 metres, about 14 feet 9 inches high, and about 25 cubic metres in capacity, with a diameter of 2·65 metres, say 8 feet 8 inches at the top, 1·8 metres, say 5 feet 11 inches at the base, and 3 metres, say 9·84 feet in the centre. Their bottom consists of a busk formed by two incline ! planes ending in two wide discharging orifices. The phosphate rests on iron bars, supported at one of their ends by the inclined planes of the busk and at the other by the horizontal metallic lintels which form the crown of the discharging orifice. These bars form two grates at the bottom of each furnace, and they are used to regulate at will the descent of the products. It suffices to draw one to let the calcined nodules fall through the opening. They can thus be withdrawn at any point of their contact with the grate; above each grate the side of the furnace is pierced by an opening to inspect the progress of the operation. The furnaces are built of bricks or masonry; they are filled with nodules in layers of 4 inches thick which are separated by very thin layers of fuel, small coke, or anthracite. A furnace of the above dimensions yields $4\frac{1}{4}$ cubic metres of calcined phosphate in twenty-four hours. The matter thus remains in the apparatus five to six days. The roasting of a ton of nodules takes 1 cwt. of fuel costing about 5d. The nodules first go to a crusher with smooth blades; they then pass by an elevator chain of cups to the top of the building where they are dropped into an iron trough which feeds the mills underneath. The ground phosphate passes automatically to an elevator which raises them to the level of the two sifting machines between which they are fed. From the sifting machine the substance falls into a wooden reservoir fitted with two bagging-up machines. Whilst in the Pas de Calais phosphates are always washed after simple hand sorting from the bulk of the gangue, in the Meuse and Ardennes they are now beginning—

after disintegration by the pick and breaking up on the spot—to screen them by throwing them on a trellis of iron wire called a *billard*, the square meshes of which are 8 to 20 mm., or a screen of iron bars 8 to 10 mm., say one-third to two-fifths inch apart, so as to free them from one-third or sometimes one-half of their impurities, but at the same time small nodules and fragments broken off by shock are lost. This method is profitable when the nodules are not friable, and easily separated from their gangue. Screening is followed by washing with a current of water in mechanical washers, or in washers fitted with blades, or dry sorting known as *fanage*. The phosphate nodules occur near the outcrop of the Greensand at a shallow depth, and the sock of the plough often brings them to the surface. An extensive business is done in collecting them and selling them in bulk to the phosphate cleaners. Fanage consists in passing the raw material through a screen after exposure to the air, so as to dry it completely and thus render the argillaceous sands more easily separated from the nodules. The operation is repeated five or six times so as to get a satisfactory cleaning. Drying is facilitated by spreading the nodules in a thin layer on the ground and turning them like hay, and from that comes the name given to the process. Fanage only succeeds if the gangue lends itself to the process. The *nodules fanés*, poorer than washed nodules, contain 10 to 15 per cent of impurities. They are exposed to rain to wash the impurities away as mud. Fanage is completed by rapid washing.

Sorting and Sale of Raw Phosphates.—Raw phosphates are sold by P_2O_5 content. They are bagged up into 5 grades each differing by 5 units—50-55, 55-60, 60-65, 65-70, 70-75, 75-80 per cent. It is thus easy to supply any strength required. To control strength of wagon loads, buyer's and seller's agents take counter scaled samples at station from each wagon, four random samples from 25 to 30 bags. One is tested by seller's chemist, the other by the buyer's. When there is more than 2 per cent between the results, the third sample is analysed by a third chemist and the average of the nearest taken. The fourth sample is kept as a check. In case of shipment the goods are sampled in the wagons as they reach the harbour. Sampling is done either by the broker alone or by the broker in presence of the seller's agent.

Different Methods of Strengthening and Utilizing Poor Quality Phosphates.—Numerous methods have been suggested to utilize the large quantities of low grade phosphates unfit for making superphosphates. These methods consist of (1) To fortify them in various ways; (2) To free them from the sesquioxides of iron and alumina, or (3) To increase their solubility or to extract from them their phosphoric acid. But none of these processes have been adopted in actual practice, because they are too costly and incompatible with

the present state of the manure trade, and they will continue to be so as long as high grade phosphates, with a low oxide of iron and alumina content, are available, which only require to be rendered soluble to produce excellent superphosphates. The following are the chief patents taken out for this purpose :—

1. *Dumonceau and Nicolas* (French patents Nos. 201,427 and 201,461) seek to fortify low grade phosphates, consisting of phosphate of lime and carbonate of lime, by the use of sulphur. The principle of the two methods is as follows: Phosphatic chalk is calcined so as to obtain a mixture of phosphate of lime and quicklime, which is mixed with water and sulphur in iron pans. The insoluble phosphate of lime is separated from the soluble sulphides formed. The strength is thus fortified 20 to 30 per cent. A current of carbonic acid is injected into the solution, and sulphur and sulphuretted hydrogen separated, the latter being converted into sulphur by sulphurous acid.

2. *Simpson* replaces sulphur by sulphuretted hydrogen (German patent 58,925), and after calcination of the raw phosphates, injects it into water, holding the phosphates in suspension. The calcium sulphides are afterwards treated by carbonic acid, or by sulphate of soda, to transform them into gypsum and sulphurous compounds; the latter treated by carbonic acid yield sulphuretted hydrogen and soda.

3. *Brochon* (French patent 215,577) extracts phosphates rich in carbonate of lime by carbonic acid under pressure after crushing and stirring up with water. The liquid containing the acid carbonate of lime is separated from the insoluble phosphate and treated for the recovery of the carbonic acid. But carbonate of lime is only feebly soluble in carbonated water even under pressure (1 cubic metre of water only dissolves 3 kg. (or 100 gallons, 3 lb.) under a pressure of 4 atmospheres at 5° C.). The process is thus too costly.

4. *Winsinger*, to prepare bicalcic phosphate free from oxide of iron, completely soluble in citrate of ammonia (German patent No. 51,739), extracts all the phosphoric acid of the phosphate of lime by sulphuric acid, converts half the solution into monocalcic phosphate, by carbonate of lime and milk of lime, which precipitate iron; he adds this precipitate to the other half, and obtains by addition of sodium sulphate, sodium carbonate and quicklime, phosphate of lime insoluble in water free from oxide of iron, which he finally adds to the solution of monocalcic phosphate. A bicalcic phosphate is thus obtained, and gypsum and caustic soda as bye-products. This process is rather complicated.

5. *O. Iahne* (German patent 57,295) prepares phosphate of lime free from oxide of iron, alumina and silica, by acting on phosphates rich in oxide of iron and alumina, by sodium bisulphate. The raw phosphates (coprolites, etc.) treated with an aqueous solu-

tion of sodium bisulphate, carbonate and phosphate of lime, dissolve whilst the silica, and iron, and alumina compounds remain insoluble, and may be separated by filtration along with the gypsum. By evaporating the solution a yellow salt is obtained, the composition of which corresponds to the formula $2Na_2SO_4 + CaH_4P_2O_8 + H_2O$, which may be employed as such, as a manure, or mixed with gypsum, horn meal, peat; it may also be used in stables, to fix ammonia.

6. In making superphosphates, *Martin* proposes to use the acid sulphate from manufacture of nitric acid. The acid sulphate from the cylinders is dissolved in water, so as to get a solution of 45° to 50° B. The precipitate consists of bisulphate, which it is easy to convert into sulphate by recrystallization, whilst the strongly acid solution is used to dissolve raw phosphates. All the phosphoric acid is dissolved, and the resultant superphosphates have less tendency to retrograde than those made with sulphuric acid of 50° to 53° B.

7. *Thonnar and Huxton's* Belgian patent No. 96,109, and *Rolland's* Belgian patent 196,190, to eliminate the oxides of iron and alumina, may also be mentioned.

8. *Schucht* proposed to make superphosphates from ferruginous phosphate thus: As soluble oxides of iron induce retrogradation of the phosphoric acid in superphosphates, whilst protoxides are inactive, and as sulphate of ammonia possesses the property of forming with protoxides of iron readily oxidizable in the air double salts very stable in air, Schucht, on such data, proposed to dissolve phosphates in presence of sulphate of ammonia, then to effect the reduction and so obtain very stable superphosphates of ammonia. With this end in view, the finely ground superphosphates are mixed with sulphate of ammonia. One part Fe_2O_3 requires 1·75 per cent of that salt to form the double salt $FeSO_4 + (MH_4)_2SO_4 + 6H_2O$. Reduction can only be effected by weak sulphurous acid which is injected under pressure into the diluted mixture of superphosphate heated to 80° to 100° C. Schucht thinks that the small amount of sulphurous acid in the product will quickly oxidize and become innocuous to plant life. The author is not aware if this method has ever been used; in any case, Schucht makes no mention of it in his book. Besides, a phosphate containing 3 to 4 per cent of sesquioxide of iron and alumina will only cause an inversion of 0·50 per cent in stored superphosphate, a loss say of 1d. a cwt. That is why the above process scarcely merits attention, except perhaps in those cases where the purchaser also pays for nitrogen. Otherwise the process would hardly be worth the trouble.

9. *Carr's* process dealing with phosphates rich in oxides of iron and alumina is analogous. It consists in calcining the phosphate, grinding it fine and then mixing 1000 parts with 400 parts of sul-

phate of ammonia dissolved in 400 c.c. of hot water, and then to add 800 parts of sulphuric acid of 53° B. A violent reaction ensues, the mass intumesces and heats to 110° C. After an hour it solidifies and is easily ground; it contains 18 per cent of phosphoric acid, two-thirds of which are soluble in water. This process is interesting; moreover, it is simple, and yields good results; it might be advantageous to use it in the manufacture of phosphate of ammonia, if the raw materials were to be got cheap. Besides, this process seems to preclude the retrogradation of the soluble phosphoric acid.[1]

10. *Glaser* manufactures precipitated phosphates from insoluble phosphates of alumina, by treating the latter with a cold alkaline solution or with a hot concentrated solution of alkaline carbonate. In this operation the phosphate of alumina is dissolved. In using the alkaline solution, the liquid separated from the residues is treated with carbonic acid. If a hot solution of alkaline carbonate be used, it is cooled, and the dissolved phosphate of alumina is precipitated. The solution is then used for a new operation. But from tests made, raw phosphate of alumina does not dissolve in a hot solution of alkaline carbonate.

11. *Petermann* of Gembloux recommends treating the raw phosphate at a high temperature, to convert the phosphoric acid into a very soluble form. Bazin has based a British patent No. 15,237 on this principle. He heats phosphates in retorts to a temperature of 1300° to 1500° C.

12. *Hodgkins* (American patent No. 423,320, 1890) mixes the phosphate in fine powder, with quicklime, which he then slakes. But it is not easily seen how that treatment can render phosphates more soluble. Besides, no field experiments appear to have been made to bring out the value of the resultant manure.

Manufacture of Precipitated Phosphate by Electrolysis.—A new method of manufacture, based on electrolysis, has been invented by Prof. W. Palmer of Stockholm. It consists in converting the raw phosphate by the wet way into a readily assimilable form, and that at the ordinary or a slightly elevated temperature. The raw material is ground apatite. It need not be finely ground. In an apparatus specially constructed for the purpose, a solution of chlorate or perchlorate of soda is electrolyzed, which disengages free chloric acid, sometimes even perchloric acid, in the *anode* cell. The acid *anode* liquid is made to react on the raw phosphate in a battery of wooden cases, fitted with perforated bottoms, so that the solvent first comes in contact with almost exhausted apatite. The alkaline liquid from the *cathode* is added to the saturated

[1] But it is evident on the face of it that such generalizations are futile. The data given can only have been applicable to the particular phosphate to which Carr applied it. All phosphates rich in oxides of iron and alumina would not respond to such treatment so as to yield the above results.

solution, in special precipitation vats, taking care to stir, until a slightly acid reaction ensues. There is thus formed crystalline precipitate of acid phosphate of lime bicalcic. It is freed as completely as possible from the mother liquor, by filtration and washing, which is greatly facilitated by the solubility of the phosphates. The yield is very satisfactory, because only about 1 per cent of the phosphate in the raw material remains in the solution. The latter, which contains a third of the amount of lime originally eliminated from the apatite, is mixed with the residual alkaline cathode liquid, and the greater part of the lime is precipitated as hydrate; finally a current of carbonic acid gas is injected. After precipitating the lime the solution is withdrawn and run into the electrolyzer. The electrolyte is thus continuously regenerated. The product so obtained generally contains 36 to 38 per cent of total phosphoric acid (the formula $CaHPO_4 + 2H_2O$ requires 46·07 per cent of P_2O_5). About 95 per cent of the phosphoric acid is soluble in Petermann's solution of ammoniacal citrate of ammonia. The composition of the product depends, moreover, on the amount of lime in the raw material; when it is rich in lime it requires a greater amount of acid, and consequently of electric energy. There is a bye-product of slaked lime equal to 33 per cent of the bicalcic phosphate formed. This process, which was the subject of several years' laboratory work, was applied industrially last year [? 1909] in an installation of 6 to 8 electric horse-power. One electric horse-power can produce annually 20 cwt. of bicalcic phosphate soluble in citrate, or 23 cwt. of 32 per cent. The cost of manufacture has been provisionally estimated at 8·44 Swedish crowns per cwt. These figures refer to an annual production of 2200 tons of bicalcic phosphate of 34 per cent. Comparative experiments on oats cultivated in pots and continued for five years, show that the phosphate precipitated by electrolysis, provided that its composition responds to that of bicalcic phosphate, exerts as energetic a fertilizing action and as durable a one as superphosphate. The addition of important amounts of carbonate of lime has not diminished the assimilability of the former, whilst with tribasic phosphate the contrary is the result.

CHAPTER IV.

HISTORICAL REVIEW OF SUPERPHOSPHATE MANUFACTURE.

It can be safely asserted that the superphosphate industry is the issue of Liebig's theory. He was, in fact, one of the first to recommend restoring to the soil, not only the nitrogen removed by crops, but also the mineral matter, more especially phosphoric acid. For this purpose he recommended the use of bone dust, and also of phospho guanos. But having remarked that the phosphoric acid of these substances only acted very slowly, he advised that they should be treated by sulphuric acid so as to render the phosphoric acid soluble, and immediately assimilable by plants. His method was adopted, and yielded remarkable results, thus giving birth to the superphosphate industry which spread rapidly in Germany, Great Britain, and France.[1]

The Manufacture of Superphosphates from 1850 *to* 1870.—It is interesting to follow the new industry in the different phases of its evolution. The theory of superphosphate manufacture is in itself very simple. Raw phosphates contain phosphoric acid. as tribasic phosphate of lime, insoluble in water, and consequently not assimilable by plants. The task of the manufacturer of superphosphate consists, therefore, essentially in converting the insoluble phosphoric acid of raw phosphates into water soluble or citrate soluble phosphoric acid. This is done by treating them with sulphuric acid, which removes. as gypsum, two parts of the lime, with which the phosphoric acid is combined, leaving one part of the lime combined with the phosphoric acid, as the monobasic or acid phosphate of lime soluble in water. The product so converted is called superphosphate, i.e. superior phosphate.[2]

[1] The writer has no intention of disparaging Liebig's claim to the treatment of bones by acid; but the treatment of coprolites and mineral phosphate by acid was first suggested by the Rev. Mr. Henslow. Mr. Lawes was either present at Mr. Henslow's lecture or read a report of it, and took out a patent for the process and proceeded to interdict Mr. Purser for digging for coprolites on his (Mr. Purser's) own land for the purposes of treating them by acid so as to dissolve them. Long litigation ensued, afterwards settled amicably. Lawes established a factory at Deptford and Purser at Millwall, with the river Thames between them. Purser's Millwall factory was closed in the early nineties. Lawes' manure factory is now at Barking. The mineral superphosphate industry is a British-born industry, like sulphuric acid manufacture.—Tr.

[2] This etymology is hardly satisfactory. *Super* here is not an abbreviation

As regards the simplicity of the process, the installation of the first superphosphate factories was very primitive. They contained little or no machinery. Three sheds, one to cover the raw phosphates, the other the den in which to dissolve the phosphate, and the third the superphosphate. So much for the factory. The tools in the beginning consisted of a few harrows, hoes, rakes, and a sieve called a screen—that was all. As to the indoor installation, it included a sulphuric acid tank, a few lead-lined measuring tanks, and three or four rectangular round or square dens. These dens were first made of brick steeped in boiling tar; afterwards cast-iron cases one inch thick, and sunk in the ground, were used. The method of manufacture was the following. A certain amount of sulphuric acid of 50° to 52° B. was run into the den; at the same time the phosphate was weighed and heaped on the edge of the den. Three men, each armed with a rake, agitated the acid, whilst the third gradually shovelled in the phosphate. The mass soon thickened, and even set before the "mixing" was complete. Nevertheless, to obtain a homogeneous mixture the mass was triturated by bringing it from one side of the den to the other; finally it was filled into barrows and shifted into the superphosphate shed. There it lay in heaps for a month; finally it was hand screened and sent out to customers. When well dissolved, it gave no core, any lumps being crushed by the back of the shovel, until sufficiently fine to pass through the screen. By such simple means sufficiently dry superphosphates were obtained, comparatively fine and well dissolved. These methods sufficed then, because the very pure raw phosphates were delivered in the ground state, or at least sufficiently fine to pass through the screen.

1871 *to* 1880.—As raw phosphates, spent bone black from sugar works, and guano from the Pacific Islands, Baker, Jarvis, etc., were chiefly used. From 1871 Mejillones guano began to be used, and then the first difficulties in the manufacture began. The larger factories then installed flatstone mills, roller mills, or stamp mills. This equipment, however, soon became defective when it was a question of working mineral phosphates such as Canadian or Norwegian apatite, Sombrero, Navassa, Curaçoa and Aruba phosphates, Mexican guano, rock phosphate, bone ash, etc. Powerful crushers were then added to the flatstone mills, for it was soon found that fine grinding played an important part in dissolving the phosphate, and in drying the superphosphate. At the same time, the need was felt for a mechanical crusher and sifter for the superphosphate. It was thus that the crusher called Carr's disintegrator was adopted.

of *superior*, but is the Latin word *super* used to show that in superphosphate the ratio of phosphoric acid to the lime is in excess of that in the normal tribasic phosphate. *Super* in fact has the same meaning here as in supersaturate, superheat. It has nothing whatever to do with quality.—Tr.

This machine did not at first always and everywhere give the result expected; the superphosphates unless suitably dissolved were converted into paste. Such was the state of affairs about 1880. But to follow up the treatment of the phosphates: At the outset of the manufacture of superphosphate, the manufacturer was himself his own chemist; he submitted his raw phosphates to a series of dissolving experiments, varying the quantity of acid each time. He then sent samples to an analyst of the superphosphates which appeared to have succeeded best, then he applied to the stock of phosphates the treatment established by groping in the dark. Each new raw material required fresh experiments. It is hardly necessary to remark that such a method of working was fertile in disagreeable surprises for the manufacturer.[1]

1880 *to* 1894.—In spite of the good quality of the raw phosphates, and their low percentage of oxide of iron and alumina, hitches in manufacture were frequent, and gradually the need was felt for a permanent control. Thus since 1880, factories of any importance have each a chemist whose duty it is to follow the material throughout all the phases of its treatment.[2] This control became more urgent when it was observed in certain mixed manures, that a certain amount of the phosphoric acid had retrograded, that is to say, it had returned to the condition insoluble in water. At the same time the use of Canadian and Norwegian apatite, and Florida and other mineral phosphates, gave off chlorine and fluorine compounds highly injurious to the health of the workmen, and annoying to the neighbourhood. The machine for mixing the acid with the phosphate was then substituted for the treatment in the open den. The first machine of this nature was an inclined cylinder, in which a shaft fitted with blades arranged in a helicoid manner revolved; it was charged with acid and phosphate at the top end, and the mixture was run out at the lower end. Afterwards this apparatus was replaced by a flat mixer of cast-iron, likewise furnished with an agitator, and in which the acid and phosphate were agitated two to three minutes, then run out into a truck underneath, whilst the gas given off by the phosphate was led out on to the roof through a wooden chimney. These machines answered all requirements so long as only guano or other phosphates rapidly attacked by sulphuric acid were being treated; however, the products were generally awanting in porosity because the greater part

[1] It would be possible to name several British manure manufactories the work of which was controlled by chemists 15 to 20 years prior to 1871, and flat stone mills were also in use prior thereto. The writer has handled works, laboratory journals of the early fifties, which show the manufacture was even then under strict chemical control by qualified men on the spot. British manure patent literature of the earlier days speaks for itself.—Tr.

[2] See above note.

of the carbonic acid was disengaged owing to a too long stay in the mixer. Then the system of closed chambers or dens was adopted, because in dissolving very hard mineral phosphates, such as Canadian apatite, pebbles, Florida phosphate, etc., a higher temperature was required, which it was easier to attain and maintain in the closed chamber, where the superphosphate remained for about twelve hours; further, because in connecting it with a well-constructed flue for the disengagement of the acid vapours, the health of the workmen was safeguarded. When the chamber possesses two flues for the disengagement of gas each 1 metre (3·28 feet) wide, and when these flues are each fitted with a fan, and can be put in connexion with the chimney stalk of the factory at will, or with a condensation plant, it is easy to eliminate steam and acid gases. A more dry superphosphate is thus obtained, and during the emptying of the chamber or "house" the workers can enter without running the risk of getting "gassed". But in actual practice hitches frequently occur. As already mentioned, as far back as 1880 it was necessary to instal plant to condense the gaseous chlorine and fluorine compounds; they consisted mostly of wooden or masonry towers drenched with water, by a Koerting's vaporizer. The hydrofluosilicic acid obtained under these conditions can be converted into silico-fluoride of sodium, the selling price of which covers the cost of condensation, and leaves even a slight margin. This product, unfortunately, has only a limited use, and ends by becoming cumbersome. The mixer installed above the closed "dens" or "houses" is that of Lorenz, which is universally used.[1] Lately, dissolving chambers have been installed at a higher level, and belt conveyors passed underneath to facilitate emptying. This system has been adopted by certain factories.

1895 *to* 1908.—Such was the situation from 1880 to 1894. Superphosphate factories possessed mills, machines for mixing acid with phosphate, installed above a closed den, into which the mixture is discharged and left to itself for twelve hours; arrangements for elimination and condensation of acid gases, disintegrators, or roller mills, armed with teeth for grinding superphosphates. Meanwhile ball mills appeared, then ball mills combined with tube crushers, then Griffin's pendulum crusher, etc.; dust chambers, on different plans, were installed; new systems of transport, such as ærial conveyors, belt conveyors, to bring the phosphate to the crushers, coal to the boilers, the crushed and screened superphosphate to the storehouse. The adoption of ærial conveyors was a real step in advance in the superphosphate industry, for independently of the economy in hand labour, they enabled the superphosphates to be thrown on the heap from above, thus ensuring the good preservation of the product. The installation of ærial con-

[1] Possibly on the continent, but not in Great Britain.—Tr.

veyors (with a useful effect of 85 per cent) inaugurated a new era in the manufacture of superphosphates. It is closely connected with electricity, the ingenious applications of which allow the use of mechanical equipment in all parts of the factory where it would be impossible to erect shafting. Electricity and ærial conveyors form a sort of connecting link between the different appliances in the factory, and contribute greatly to their increased output. Electric light spreads cheerfulness in all directions; the electric motors driven from a central station work silently in the most distant parts of the factory, the different organs of which thus work in perfect harmony. A vexed question is that of knowing the treatment to which superphosphates should be subjected from the moment it is shifted from the den, so as to obtain in the most simple and the most rapid manner a good product which will keep well. To solve it, numerous processes have been elaborated, all converging to the same end, which is to secure a dry pulverulent phosphate easily distributed by the drill sowing machine. The point of departure of these researches was Florida phosphate, which from 1880 [? 1890] was and still is one of the most important raw materials of superphosphate factories, afterwards the phosphates of Tennessee, Algeria, and Tunis. Superphosphates made from Florida phosphate are distinguished by a high percentage of free phosphoric acid which gives them a damp feeling when touched. The most simple means of remedying this inconvenience consists in drying them, and thus quite a series of driers have been constructed for the purpose. At the present time all superphosphates, and especially those intended for export, are dried. But it was soon observed that if drying diminished the percentage of moisture in the superphosphate, it increased their percentage of free phosphoric acid, and of hydrofluosilicic acid, and in such conditions, whilst appearing dry, they possessed the property of attracting moisture and attacking the canvas of the bags.[1] In 1896, it was found that degelatinized bones, and more recently Gafsa phosphate, afforded simple means of drying superphosphates and rendering them pulverulent without exposing them to retrogradation. This point will be reverted to in the sequel. At the same time several specialists in this kind of work, independently of each other, have tried to find methods of obtaining good superphosphates whilst imparting great rapidity to the working process. In this way the grating machine was invented (Heymann and Nitsch's process). But experience proved that perfect results could only be obtained by finely dividing the superphosphates from the mixing den and by diminishing their free acidity. This result has been fully obtained. Owing to improved equipment, means are available of producing from all raw

[1] Steeping in gum kino extract is found in Australia to render manure bags rot proof.—Tr.

phosphates, superphosphates which answer all requirements since it has been recognized that dryness and the pulverulent state of the superphosphates depends in the first place not on their percentage of moisture but on their free acid content. The recently discovered phosphates of Christmas Island and Ocean Island likewise enable phosphates with 20 to 21 per cent of phosphoric acid soluble in water to be produced. Thus, as already observed, it is Florida phosphate which has been the occasional cause of the methods of working which we have just enumerated. This same phosphate more than any other has put chemists to the test owing to its high percentage of oxide of iron and alumina, which are the great enemies of superphosphate manufacturers. The retrogradation of the soluble phosphoric acid caused disagreeable surprises for the chemist and manufacturer, and if the means of prevention be not possessed by a factory working on the large scale, the causes and conditions under which they are produced have been determined. Chemistry, the inseparable companion of industry, has taken a considerable part in the progress realized in superphosphate manufacture from its birth to the present time. Chemists are attached to all manure factories; to them belongs the merit of freeing this industry from empiricism so as to establish it on a truly scientific basis. French chemists have had a large part in the development of the manure industry. Their learned researches joined to that of French geologists have greatly contributed to the realization of the value of the French phosphate deposits, the immense reserves of which will suffice for a long time to cover the requirements of French agriculture.[1]

[1] That we in Great Britain have not a voluminous special literature dealing with the chemistry of manure manufacture, in no way detracts from the merits and claims of British agricultural and manure works chemists. Our Patent Office records prove that they have been first in the field in all branches of research in this domain. Both French and German current methods of precipitated phosphate manufacture, double superphosphate manufacture, and such like, are all borrowed from British patents like those of Professor Way, Benjamin, Tanner, etc., away back in the sixties and seventies.

CHAPTER V.

THEORY OF MANUFACTURE OF SOLUBLE PHOSPHATES.

It has already been seen that to render the phosphoric acid in raw phosphates soluble, when it exists as tribasic phosphate of lime $Ca_3(PO_4)_2$, it suffices to replace [each of] the two atoms of dyad calcium by two atoms of hydrogen by means of sulphuric acid, the monobasic phosphate of lime, or acid phosphate of lime $CaH_4(PO_4)_2$, soluble in water, the calcium displaced by sulphuric acid forming gypsum $CaSO_4 2H_2O$, according to the following equation :—

$$Ca_3(PO_4)^2 + 2H_2SO_4 + 5H_2O = CaH_4(PO_4)^2H_2O + 2CaSO_4 2H_2O$$

Tribasic phosphate of lime.	Sulphuric acid.	Water.	Monocalic phosphate.	Sulphate of lime.
310	196	90	252	344
596			596	

As the equation shows, the sulphuric acid used is sulphuric acid which has not been concentrated, that is, it contains a certain amount of water incidental to its manufacture. This water assists in the crystallization of the two new compounds formed, monocalcic phosphate and gypsum ; it, moreover, assists in thinning the mixing and thus facilitates decomposition. In fact, if the mass formed by the mixing of phosphate and acid be too thick, the new salts, especially gypsum, would set and harden rapidly and thus bury a certain amount of the raw phosphate which would escape the action of the acid. Gypsum forms, as it were, the skeleton of the superphosphate. But the conversion of raw insoluble phosphate into soluble phosphate is not accomplished in such a complete and adequate manner as the equation appears to indicate. Experiments have proved that the insoluble phosphate is rendered soluble in two somewhat parallel stages. The first yielding free phosphoric acid and gypsum only extends to two-thirds of the tricalcic phosphate. In the second the free phosphoric acid acts on the remainder of the tricalcic phosphate, and combines with it to form acid phosphate of lime or monocalcic phosphate.

(1) $3Ca_3(PO_4)^2 + 6H_2SO_4 + 12H_2O = 4H_3PO_4 + Ca_3(PO_4)^2 + 6(CaSO_4 + 2H_2O)$
Calcium phosphate. Sulphuric acid. Water. Phosphoric acid. Tribasic phosphate. Gypsum.

(2) $4(H_3PO_4) + Ca_3(PO_4)^2 + 3H_2O = 3[CaH_4(PO_4)^2 + H_2O]$
Phosphoric acid. Tribasic phosphate. Water. Monocalcic phosphate. Water.

One can demonstrate the soundness of this equation by treating after equation (1) 310 parts of tribasic phosphate of lime with 196 parts of monohydrated sulphuric acid and 90 parts of water, diluting the mass rapidly with water and filtering quickly. Two-thirds of the phosphoric acid are then present in the filtrate in the free state. But if the mass be only diluted after it has set, all the phosphoric acid exists in the filtrate as monocalcic phosphate. The explanation is that phosphoric acid is a much weaker acid, and acts much more slowly than sulphuric acid, and that is why the reaction of equation (2) is accomplished more slowly than equation (1). If an insufficient amount of sulphuric acid be used for conversion, only bicalcic phosphate is obtained.

$$Ca_3(PO_4)^2 + H_2SO_4 + 6H_2O = Ca_2H_2(PO_4)^2,4H_2O + CaSO_42H_2O$$

In this conversion, a portion of the tribasic phosphate of lime is transformed first into monocalcic phosphate $CaH_4(PO_4)^2$, but that re-combines with the remainder of the tribasic phosphate of lime.

$$\underbrace{CaH_4(PO_4)^2,H_2O + Ca_3(PO_4)^2 + 7H_2O}_{252 \qquad 310 \qquad 126 \qquad 688} = \underbrace{2Ca_2H_2(PO_4)^22H_2O}_{688}$$

But the free phosphoric acid makes the superphosphate damp, pasty, and unfit for distribution (passing through the drill, etc.) in that condition. If the raw phosphate be rendered soluble, by hydrochloric acid or by nitric acid, no free phosphoric acid is obtained, but merely acid phosphate of lime, very soluble in water. Dry superphosphates can be obtained in that way. But such acids are less abundant and much dearer than sulphuric acid. However, hydrochloric acid when it is to be had cheap, is sometimes added in the proportion of 10 per cent to the sulphuric acid. But the phosphate is not rendered soluble by pure hydrochloric acid, as that would give rise to calcium chloride, which is highly deliquescent, and cause the superphosphate to be damp and unsaleable. Moreover, calcium chloride is injurious to vegetation when present to any great extent. In presence of sulphuric acid, the calcium chloride is again converted into calcium sulphate and hydrochloric acid, which assists in dissolving the phosphate.

From the following equation the quantities of sulphuric acid and water required to dissolve a given amount of phosphate may be readily calculated :—

$$\underbrace{Ca_3(PO_4)^2}_{310} + \underbrace{2H_2SO_4}_{196} + \underbrace{5H_2O}_{90} = \underbrace{CaH_4(PO_4)^2H_2O}_{252} + \underbrace{2(CaSO_4 2H_2O)}_{344}$$

$$\underbrace{\qquad\qquad\qquad\qquad}_{596} \qquad\qquad \underbrace{\qquad\qquad\qquad\qquad}_{596}$$

In this connexion it will be well to bear in mind that the symbols indicate not only the elements but precise and accurately determined quantities. Thus the formula for water (H_2O) indicates not only that water is composed of the two elements, hydrogen and oxygen, but also that it results from the combination of one atom of oxygen with two atoms of hydrogen. As the atomic weight of hydrogen = 1, and that of oxygen = 16, it will be at once seen that eighteen of water consists of two of hydrogen and sixteen of oxygen. These figures apply just as much to grams as to tons. The following is a similar calculation for phosphates, thus tribasic phosphate of lime contains :—

	Atomic Weight.
Calcium (Ca)	= 40
Phosphorus (P)	= 31
Oxygen (O)	= 16

1. A molecule therefore of $Ca_3(PO_4)_2$ weighs :—

$$\begin{aligned} Ca_3 &= 40 \times 3 = 120 \\ P_2 &= 31 \times 2 = 62 \\ O &= 16 \times 8 = 128 \\ &\qquad\qquad 310 \end{aligned}$$

2. A molecule of sulphuric acid H_2SO_4 (H = 1 ; S = 32 ; O = 16) = 2 + 32 + 16 × 4 = 98. But tribasic phosphate of lime requires two molecules of sulphuric acid to render it soluble ; we thus get 2 × 98 = 196 of sulphuric acid and 5 × 18 = 90 of water. Sulphuric acid may be calculated as SO_3 and H_2O, say as the hydrate of sulphuric acid and water. To render the phosphate soluble 5 + 2 = 7 molecules of water are required. It follows, therefore, in order to dissolve 310 parts of tribasic phosphate of lime, that these 310 parts of $Ca_3(PO_4)_2$ must be put in contact with 160 parts of SO_3 and 126 parts of water. One part (say one ton) of $Ca_3P_2O_8$ requires therefore $\frac{160}{310} = 0{\cdot}516$ parts SO_3 and $\frac{126}{310} = 0{\cdot}406$ parts water.

$$\begin{aligned} 100 \times 0{\cdot}516 &= 51{\cdot}6 \text{ parts } SO_3 \\ 100 \times 0{\cdot}406 &= 40{\cdot}6 \text{ ,, } H_2O \\ &\qquad\qquad 92{\cdot}2 \qquad H_2SO_4 \end{aligned}$$

Now as 92·2 parts of H_2SO_4 contain 51·6 parts of SO_3, 100 parts contain $\frac{51{\cdot}6 \times 100}{92{\cdot}2} = 55{\cdot}96$ SO_3. It is, therefore, acid containing 56 per cent of SO_3 that has to be used. By consulting the table by Lunge and Isler, at the end of the book, it will be found that acid of that strength has the specific gravity of 1·600 = 54° B. or 120° Twaddel. But in actual practice it happens that the acid used is more concentrated or more dilute. Suppose that the acid marked 60° B., according to the table above mentioned, contains 63·7 per cent SO_3, it will, therefore, be necessary to use $\frac{51{\cdot}6 \times 100}{63{\cdot}7} = 81$ parts to render 100 parts of tribasic phosphate of lime soluble, and it would be necessary to add the required amount of water thereto. If the acid weighs less than 54° B., say 50° B., the same calculation is made. Acid of 50° B. contains 51·04 per cent SO_3 of acid of that strength, therefore it would be necessary to use $\frac{51{\cdot}6 \times 100}{51{\cdot}04} = 101$ parts for 100 of $Ca_3P_2O_8$.

Effect of the Impurities in Phosphates on their Behaviour in the Process by which they are Rendered Soluble.—But raw phosphates, moreover, contain several other compounds besides tribasic phosphate of lime—such as carbonate of lime, oxides of iron, and alumina, calcium fluoride, decomposable silicates, etc. If, therefore, only the amount of sulphuric acid required for the phosphate were taken, the latter would not be rendered completely soluble, because the sulphuric acid would first attack the carbonate of lime and then the tricalcic phosphate. It is thus necessary to determine the percentage of these ingredients in the phosphate and allow for them in calculating the acid.

Carbonates of Lime and Magnesia.—In treating phosphates with sulphuric acid, the carbonates are attacked first. It is generally a question of carbonate of lime, as carbonate of magnesia is only met with rarely, for example in Carolina and Florida phosphates. Carbonate of lime is, therefore, dissolved at the very first, then follow the other compounds in the order of their decomposability by acid. The decomposition of the carbonate of lime and the consequent formation of gypsum which follows it at an equal pace, causes an energetic reaction, which is very favourable to the progress of the process by which the phosphates are rendered soluble. The heat disengaged re-heats the mass, the carbonic acid in its efforts to escape raises the mixture and renders it porous and spongy like a well-risen loaf in the baker's oven, and thus facilitates drying. More than 5 per cent of carbonate acts unfavourably, in this sense that leaving the expense of the extra acid [1] that it entails

[1] But the acid is *the* raw material on which the manufacturer makes his profit!—Tr.

out of account, it gives rise to an excessive amount of gypsum which brings numerous drawbacks in its train as will be seen in the sequel. The quantity of acid absorbed by the carbonate of lime in normal amount (1 part of $CaCO_3$ in tribasic phosphate of lime requires 1·5 parts of SO_3 [1]) is compensated to a great extent by the advantages got in "mixing" and by the quality of the superphosphate. Phosphates free from carbonate of lime do not heat but very poorly in contact with acid; the reaction is consequently slow, the operation takes longer and the final product is difficult to dry. To remedy this drawback in treating phosphates of this nature, apatites for example, it is best to mix them with phosphatic chalk when being ground, but the superphosphate which results is not so homogeneous as that got from the chalky phosphates of Algeria. The amount of acid required to decompose the carbonates is calculated from the following equations:—

$$\underbrace{CaCO_3 + H_2SO_4 + H_2O}_{100 + 98 + 18 = 216} = \underbrace{CaSO_4 2H_2O}_{172} + \underbrace{CO_2}_{44} \quad (216)$$

$$\underbrace{MgCO_3 + H_2SO_4 + 6H_2O}_{84 + 98 + 108 = 290} = \underbrace{MgSO_4 7H_2O}_{246} + \underbrace{CO_2}_{44} \quad (290)$$

Magnesia is also met with, but in smaller quantities, as tribasic or neutral phosphate. The following reaction then occurs:—

$$Mg_3(PO_4)^2 + 2H_2SO_4 + 16H_2O = MgH_4(PO_4)^2 2H_2O + 2MgSO_4 7H_2O$$
$$2MgHPO_4 + H_2SO_4 + 9H_2O = MgH_4(PO_4)^2, 2H_2O + MgSO_4 7H_2O$$

Acid phosphate of magnesia is not deliquescent and not decomposed by water.

Iodine.—Certain phosphates contain iodine, as calcium iodide (CaI_2), which is converted by the sulphuric acid into hydriodic acid at the ordinary temperature of the "mixing"; when the mass heats the acid reacts on the hydriodic acid, and the iodine liberated escapes as a violent vapour. Phosphoric acid has no action on hydriodic acid.

Calcium Fluoride.—Most phosphates contain more or less calcium fluoride. This substance is likewise decomposed by sulphuric acid at a temperature above 40° C. (104° F.). It is then given off as gaseous hydrofluoric acid. But the latter acts in its turn on silicic acid and forms with it silicic fluoride. These two reactions may be represented thus:—

$$CaF_2 + H_2SO_4 + 2H_2O = CaSO_4 2H_2O + 2HF$$
$$SiO_2 + 2CaF_2 + 2H_2SO_4 + 2H_2O = SiF_4 + 2CaSO_4 2H_2O.$$

[1] Evidently dilute acid of 120° Tw.—Tr.

The silicic fluoride makes itself felt by a penetrating acrid odour; it decomposes in presence of water into gaseous hydrofluosilic acid which volatilizes, and into orthosilicic acid

$$3SiF_4 + 4H_2O = 2H_2SiF_6 + SiO_2 + 2H_2O$$

Gaseous hydrofluoric acid acts on silicates to render them soluble :—

$$Al_2(SiO_3)^3 + 6HF = Al_2F_6 + 3H_2SiO_3$$
$$Al_2(SiO_3)^3 + 18HF = Al_2F_6 + 3SiF_4 + 9H_2O$$
$$CaSiO_3 + 2HF = CaF_2 + H_2SiO_3$$
$$CaSiO_3 + 6HF = CaF_2 + SiF_4\ 3H_2O$$

Ost observed that in the "dissolving" process two-thirds of the fluorine contained in the phosphates escapes as gas, whilst one-third remains as calcium fluoride; but according to Klippert 50 per cent of the fluorine is disengaged as gas, 30 per cent remaining undecomposed, and 20 per cent absorbed mechanically by the mass as SiF_6H_2. Fossil bones contain up to 16 per cent of CaF_2.

Silicates of Lime and Alumina.—The silicates $CaSiO_3$, $Al_2(SiO)_3$ are partly soluble in sulphuric acid and partly insoluble. The lime silicates in Algerian phosphate are decomposable by sulphuric acid, the silica being precipitated as a gelatinous thick swollen mass, and can thus enclose a certain amount of insoluble phosphate of lime which escapes being rendered soluble. The undecomposed silicates of alumina absorb acid mechanically and are gradually decomposed by it.

Oxides of Iron and Alumina.—The presence of oxides of iron and alumina in raw phosphates has serious drawbacks. It may in some cases prevent their use in superphosphate manufacture. The iron is present in different forms, more often as oxide combined with the phosphate, more rarely as free oxide or as protoxide (ferrous oxide). It also occurs as sulphide FeS^2 either infinitely divided, as in Tennessee phosphate, which contains as much as 4 per cent in the river pebbles of the Carolinas, in certain Belgian phosphates, or as lamellæ in the phosphates of Podolia. But sulphide of iron is generally present in too small a quantity to cause serious mishaps. Phosphates containing protoxide of iron, ferrous oxide FeO, have a greyish-black or a bluish-grey colour like certain Florida, Tennessee, and Carolina river pebbles. In the process of "dissolving" phosphates the iron compounds are decomposed more or less rapidly and completely according to the form in which they occur, according to the density (? compactness) of the phosphates, the amount and the state of concentration of the acid used, and finally according to the extent to which the "mixing" becomes heated during the re-action.

Decomposition takes place thus :—

$$3FePO_4 + 3H_2SO_4 \rightleftarrows (FePO_4 2H_3PO_4) + Fe_2(SO_4)_3.$$

If sulphuric acid be employed in excess all the phosphoric acid is liberated.

$$2FePO_4 + 3H_2SO_4 \rightleftarrows 2H_3PO_4 + Fe_2(SO_4)_3$$

The decomposition of the phosphate of iron therefore gives phosphoric acid and sulphate of iron. A portion of this sulphate of iron reacts on the acid phosphate of lime and occasions a gelatinous precipitate, whilst a small fraction remains inactive and can be detected in the aqueous extract of the superphosphate. This amount is about 2 per cent. Consequently the presence of 2 per cent of oxide of iron in (raw) phosphate has practically no bad effect, that amount remaining as soluble sulphate if the acid be slightly increased ; as much as 3 to 4 per cent of oxide of iron always causes a loss of soluble phosphoric acid. Beyond 4 per cent the phosphate becomes unfit for superphosphate manufacture. In his excellent treatise on superphosphates, Schucht insists on this special point and explains the precipitation of the phosphate of iron thus :—

$$CaH_4(PO_4)^2H_2O + Fe2(SO_4)^3 + 5H_2O = FePO_4 2H_2O + CaSO_4 2H_2O + 2H_2SO_4$$

$$H_2SO_4 + CaH_4(PO_4)_2H_2O + H_2O = CaSO_4 2H_2O + 2H_3PO_4$$

$$2(FePO_4 2H_2O) + 4H_3PO_4 = FePO_4 2H_3PO_4 + 4H_2O$$

He demonstrates the course of these reactions by the following small experiment. If one adds to a solution of a superphosphate say an acid solution of a salt of oxide of iron, phosphate of iron is precipitated. But according to their degree of concentration superphosphate solutions act differently on solutions of oxide of iron ; thus a 2 per cent solution precipitates immediately all the oxide of iron, a 4 per cent solution gives a weaker reaction, and in a 6 per cent solution the reaction occurs slowly. Consequently the greater the amount of free phosphoric acid in a superphosphate solution, the more it retains the iron in solution. If a solution of a ferruginous superphosphate be evaporated to dryness and the residue taken up with water, a clear solution is not obtained, but a solution with a considerable precipitate. This hydrated phosphate of iron may pass in the superphosphate into the completely insoluble state, when its constitutional water is removed from it by the crystallization of the amorphous sulphate of lime.

$$FePO_4 2H_2O + CaSO_4 = CaSO_4 2H_2O + FePO_4$$

This explains why an incompletely dissolved or retrograded superphosphate cannot be improved by fresh treatment with

sulphuric acid. There is then only obtained a wet tacky mass, the acid uniting with the gypsum to form $CaH_2(SO_4)^2$. It is only after a certain time, after numerous treatments followed by drying, that this free acid ends by acting on the non-decomposed phosphate, but not on the phosphate of iron. On the other hand, the hydrated phosphate of iron is soluble in the free phosphoric acid of the superphosphate, but only in a transitory fashion.

Oxide of alumina in the proportion in which it generally occurs as $AlPO_4$ in raw phosphates does not exert directly any influence on the retrogradation of the phosphoric acid. Contrary to what takes place with oxide of iron, the hydrated oxide of alumina $Al_2O_3H_2O$ does not become soluble in acid until after ignition. The hydrated phosphate of alumina as well as the anhydrous phosphate of alumina is soluble in the precipitated condition in phosphoric acid. That is why it is unnecessary to eliminate the phosphate of alumina from raw phosphate so long as it exists in normal limits. Alumina as silicate may prove injurious; if it be not decomposed by the sulphuric acid it may in certain cases cause the retrogradation of a portion of the phosphoric acid.

Organic Matter.—According to the origin of the phosphates matter is present which is carbonized in the mixing process either by sulphuric or phosphoric acid. The dust given off by certain phosphates (Algeria, Gafsa) during grinding diffuses a bad smell which it is impossible to eliminate during manufacture. Ignition alone suppresses it. Coprolites, Carolina phosphate, pebbles, Algerian phosphate give off an odour of ichthyocol or of naphthene analogous to that given off on heating petroligneous shale, limestone, etc. These odours are due to the decomposition of the remains of the fat of marine animals. More often, however, a penetrating odour is given off from phosphates, resulting from the decomposition of the remains of slightly volatile organic matter, which are not decomposed by sulphuric acid except at the high temperature incidental to the mixing process. These remains form a nitrogenized and sulphurous charcoal, which is then converted into compounds with an acrid and penetrating odour. Certain coprolites even exude a sort of tar during drying, forming up to 0·5 per cent of the mass. The above shows how variable the raw materials are which are met with in course of manufacture.

Method of Determining the Amount of Acid to use in Order to Render the Phosphate Soluble.—It was a long time before an agreement could be come to as to the quantity of sulphuric acid to use to render the raw phosphate soluble. There was a plausible reason, for the manufacturer had the alternative of completely dissolving the phosphate by the use of a large quantity of sulphuric acid, and then the superphosphate so produced was too moist to be spread by means of the drill, or of using less acid and only incom-

pletely dissolving the phosphate. The difficulty has been got over by installing superphosphate drying machines, so that there now need be no fear in using the requisite amount of acid to dissolve the phosphate completely. To calculate the acid some proceed in a purely empiric manner, by using 1 ton 4 cwt. of sulphuric acid of 50° B. for one ton of tribasic phosphate of lime, and adding the surplus of acid necessary to saturate the carbonate of lime; others saturate two atoms of calcium with 550 grammes of sulphuric acid of 50° B. and increase this quantity by that necessary to saturate the carbonate of lime and the sesquioxide, three of sulphuric acid of 50° B. for one of sesquioxide; others finally starting from the analysis of the raw phosphate, use the amount of acid necessary to saturate the sesquioxides and the total lime, less the portion of the latter inherent to the formation of acid phosphate of lime. The last method is evidently the best, seeing that it is based on theoretical figures; it was always used for treating guanos, which owing to the presence of bibasic phosphate of lime, were dissolved with the greatest ease. But as already mentioned, mineral phosphates often contain small amounts of silicates, which likewise absorb sulphuric acid. From the foregoing practical men have concluded that the best method is to make a trial mixing. These trials ought to be carried out each time on a sufficient amount of material to fill the mixer. Accordingly the phosphate and acid are mixed by the aid of the agitator and the process is conducted exactly as in normal working. The reaction, which takes place in the mixing den, does not consist solely in the heating of the materials, as one would be inclined to imagine, because if that were the case the same result would be attained by heating the sulphuric acid or even the material on which it acts when working on the small scale. In the case of certain mineral phosphates, such as Canadian apatite, mixing test trials never succeed, because the phosphoric acid formed in the first phase of the operation cannot immediately exercise its action on the rest of the phosphate. The operation drags, the substance remains pasty, the sulphuric acid attracts moisture, its action gradually becomes weaker, and, finally, a bad quality superphosphate results.[1]

It is thus necessary when new phosphates are to be used, the behaviour of which in mixing is unknown, to make trial mixings with a larger quantity of acid than that got by calculation, and to adhere afterwards to the amount which gave the best results. With

[1] A rough trial test giving useful indications may be made when new phosphates of unknown behaviour are being bought in the slack season by treating the phosphate with acid in an earthenware bread pan, not stirring too much and setting aside with the pan lid on and inspecting the result after 24 hours' standing in a warm place. If the mixture dries, then it will dry far better on the large scale.—Tr.

Florida phosphate good results are obtained by increasing the theoretical amount by 5 per cent. It is easy to understand, moreover, that the richer the raw material is in phosphoric acid the less it should be over-acidified, because the phosphates of that category generally contain little sesquioxides or silicates capable of absorbing the acid added in excess. Phosphates rich in carbonate of lime, such as Somme and Algerian phosphates, stand much acid; however, the excess of acid rarely surpasses 5 per cent of the quantity calculated according to their percentage of phosphoric acid.[1]

If the trial mixing be well conducted it gives very satisfactory results. The superphosphate obtained should be comparatively dry and porous when it is cold. After each trial the phosphoric acid, soluble in water, is determined, the free phosphoric acid and the insoluble phosphoric acid. Bone phosphates are almost completely rendered soluble. But it is not so with mineral phosphates, which always leave a small amount of insoluble phosphoric acid. This fraction amounts to about 1·4 for Gafsa superphosphate, 1·7 for Algerian, 1·4 for Peace River and Pebbles, 0·5 to 1 for Florida, 1·7 for Carolina, and 2·1 for Tennessee (Schucht). Up to now the efforts of scientists and practical men have been powerless to abolish this loss. The density and strength of the acid play a certain rôle in mixing. Phosphates rich in carbonate work best with cold acid, whilst those poor in carbonate require hot acid. It has been found, moreover, that the soluble phosphoric acid is better preserved in superphosphates prepared with acid of 54° B. than in superphosphates made with acid of 50° B.

Damp phosphates and those difficult to dissolve require stronger acid than when dry and rich in carbonate of lime.

Finally, it is well to bear in mind that superphosphates should contain a certain amount of free phosphoric acid. That has the effect of retarding the decomposition of the acid phosphate of lime in the soil, and regarded from that point of view it constitutes an indispensable element of the superphosphate.

Schucht shows in the following table the amount and the strength of acid which it is convenient to use in rendering various phosphates soluble.

[1] In the translator's experience with Somme phosphate, 60 to 62 per cent $Ca_3P_2O_8$, he found that it invariably took exactly its own weight of sulphuric acid calculated as B.O.V. He preferred to use acid heated to 150° F. Somme phosphate rises much more in the mixing den than Carolina, so that it will hold nearly twice as much Carolina super as it will of Somme super. But great care must be taken that there is no flaw in the closed steam pipe heating the acid, or the acid may gain access to the boiler. The translator had a case of this sort where the engineer, after ruining his boiler, in order to escape censure, tried to blame his well-water as being naturally acid!—Tr.

TABLE XLI.—AMOUNT AND STRENGTH OF ACID REQUIRED TO DISSOLVE VARIOUS PHOSPHATES.[1]

	$Ca_3P_2O_8$ Per cent.	Oxide of Iron and Alumina. Per cent.	Carbonate of Lime. Per cent.	100 lb. of Phosphate require lb. of Acid.	Degree Baume.[2]
Bone ash	82·1	0·3	4·4	95	52
Malden guano	72·4	0·3	12·5	82	60
Aruba phosphate	78·6	3·8	4·2	100	52·5
Curaçao phosphate	88·0	0·1	7·0	105	50
Podolia coprolites	74·7	5·0	4·7	120	50
Carolina phosphate	56·0	2·8	12·0	100	50
Canadian phosphate	76·8	3·3	6·6	110	55
Somme phosphate	67·0	3·8	10·2	105	51
Liége phosphate	55·5	3·6	16·8	105	50
Ciply phosphate	40·7	2·3	41·8	131	49
,, ,,	48·2	1·7	35·6	125	49
,, ,,	53·8	1·3	34·2	130	49
,, ,,	57·4	0·8	29·1	125	49
Florida phosphate	78·0	2·0	4·4	110	50
Pebble phosphate	68·0	1·8	6·3	100	50
Peace River phosphate	61·7	2·9	8·4	95	50
Tennessee phosphate	80·5	3·4	5·2	110	50
,, ,,	69·9	2·3	6·0	105	50
Algerian phosphate	58·2	0·5	20·8	110	50
,, ,,	65·0	0·6	16·0	100	52
Gafsa phosphate	59·6	1·7	9·7	100	50
Clipperton guano	78·7	0·1	6·7	100	52
Peruvian guano	26·2	0·5	1·8	25	60
Precipitated phosphate	32·0	—	—	55	60
Steamed bone dust	22·0	0·4	5·2	70	50
Degelatinized bone dust	31·0	—	—	74	55

[1] Such a table is of course very valuable, but it is better to calculate all acid to B.O.V. whatever be the strength used. That keeps the acid account correct. At stocktaking the manufacture then shows a gain in weight, but that is all to the good, a sort of manufacturer's own private bonus. But if the different strengths of acid used be all entered at the actual weight taken, then there can be no chemical control of the amount of acid used; nor if the manure manufacturer makes his own acid of the amount of acid he has made. The general rule is to take the stock of acid in hand, calculate it to B.O.V., add to it the amount used in mixing, and take that as the amount of acid made in the season, which, checked against the pyrites burnt, say Rio Tinto, should give a yield of 30 cwt. B.O.V. per ton of pyrites burnt.—Tr.

[2] (1) 49° B = D = 1·515 = 103 Tw. (2) 50° B = D = 1·530 = 106 Tw. (3) 51° B = D = 1·546 = 109·2° Tw. (4) 52° B = D = 1·563 = 112·6 Tw. (5) 52·5° B = D = 1·572 = 114·4° Tw. (6) 55° B = D = 1·615 = 123° Tw. (7) 60° B = D = 1·710 = 142° Tw. (8) Acid in Great Britain is generally used as near D = 1·60 = 120° Tw. as practicable. B.O.V. is acid of D = 1·700 or 140° Tw.—Tr.

CHAPTER VI.

MANUFACTURE OF SUPERPHOSPHATE.

The manufacture of superphosphate comprises three principal operations: 1. Grinding the raw phosphate. 2. Rendering the ground raw phosphate soluble by sulphuric acid. 3. The drying of superphosphate.

Grinding Raw Phosphate.—Raw phosphate should be carefully ground, because it is found that the fineness of the phosphate contributes to a great extent to a perfectly successful superphosphate. Thus the powder should not leave more than 10 per cent of residue on a 70 mesh sieve, and this residue should not exceed the size of groats; it is only at this cost that all the phosphoric acid is rendered soluble. Certain phosphates are delivered ground, others in lumps of the size of the fist. To lend itself well to grinding the phosphate should be *dry*. Florida phosphate especially should not contain more than 1 per cent of moisture, whilst Algerian phosphate grinds very well with 5 per cent of water. When dealing with phosphate drenched with sea water in transit or accidentally in the warehouse, it is extended on a drying platform of sheet iron heated by the combustion gases [over the flues from the boiler furnaces]. In the grinding of phosphate at the present day ball-mills—continuously feeding and discharging—are in general use, which owing to their strong construction and their stable working answer well for the purpose. In older factories flatstone mills are frequently used. Griffin's crusher with walking beam has likewise some rare partisans, but it is costly and requires frequent repairs which become heavy in the end. The material to be introduced into this grinding machine ought preferably to be reduced, and for that purpose edge runners are suitable. The crusher, with blades—disintegrator—is likewise used, but only to crush phosphate in large nodules or rock phosphate. These machines will now be briefly described, along with the other grinding machines commonly used in the manufacture of chemical manures.[1]

[1] But superphosphate and chemical manures generally were made in Great Britain by mechanical means for the last fifty years at least. However, if France was originally twenty years behind the times in manure manufacture, it has more than made up for it by recent progress. But Great Britain

Grinding Machines—Edge Runners.—Edge runners consist generally of two stones turning on a circular plate round a vertical shaft; at the same time each stone turns round its own horizontal axis, and grinds the material both by crushing and rubbing. The horizontal axes of the two mills are independent of one another, and each connected with the vertical shaft by means of a hinged crank. The stones can thus be raised or lowered independently the one of the other. The material is fed into the mill directly, by the shovel or by an elevator; it is drawn continually

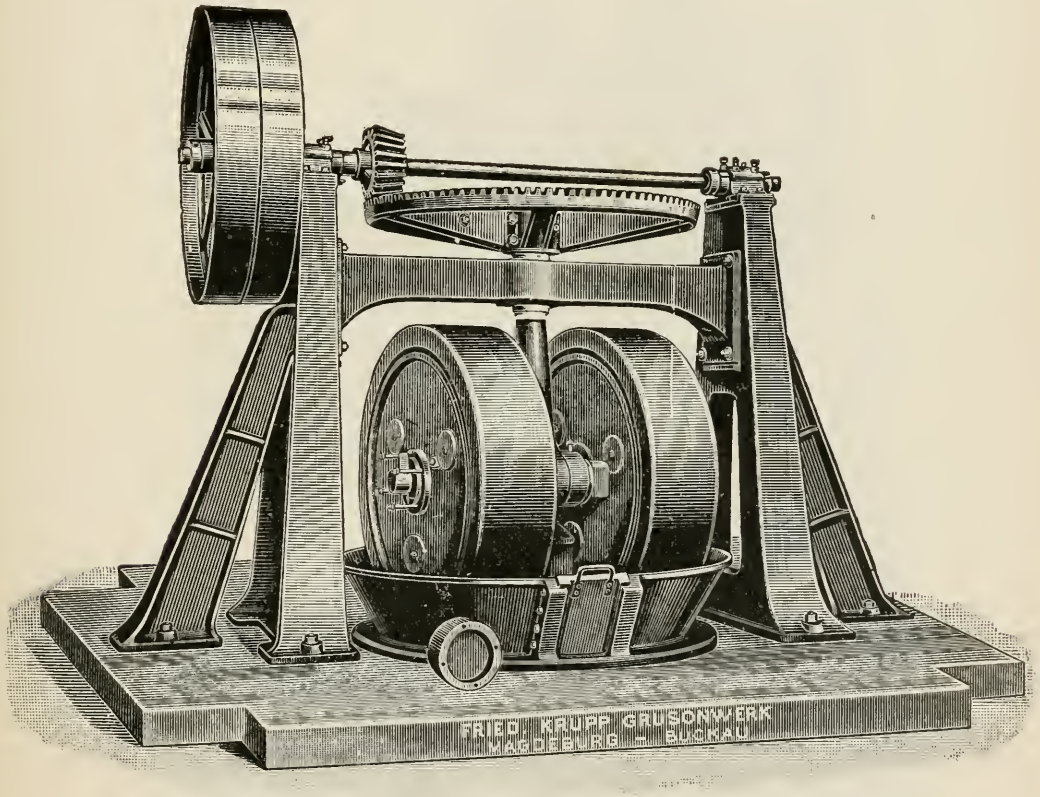


Fig. 1.—Vertical Edge Runner.

under the stones by collectors, and when it is sufficiently ground, it is evacuated by the automatic discharge, sifted and bagged up. Fig. 1 shows a pair of edge runners. Two men suffice to attend to the mill, the elevator and the sifting machinery.

Flatstone Mills.—Flatstone mills are built either with the upper stone stationary or the lower stone stationary, according as it is the upper or lower stone that revolves. Mills of the first kind are

is not standing idle. A manure work at Forres away in the "Farther North" has recently been equipped with automatic shifting machinery for removing manure from the "den".—Tr.

used for crushing very hard phosphate, those of the second kind for soft phosphates. The foundation consists of cast-iron columns or a hollow cast-iron support, on which the cage of the mill is fitted up. The shaft of the mill is sustained by a movable bearing with collar; its lower part rests in a socket. The bearing with collar is screwed to the bottom of the mill cage and completely protected from dust. The adjustment of the revolving millstone is

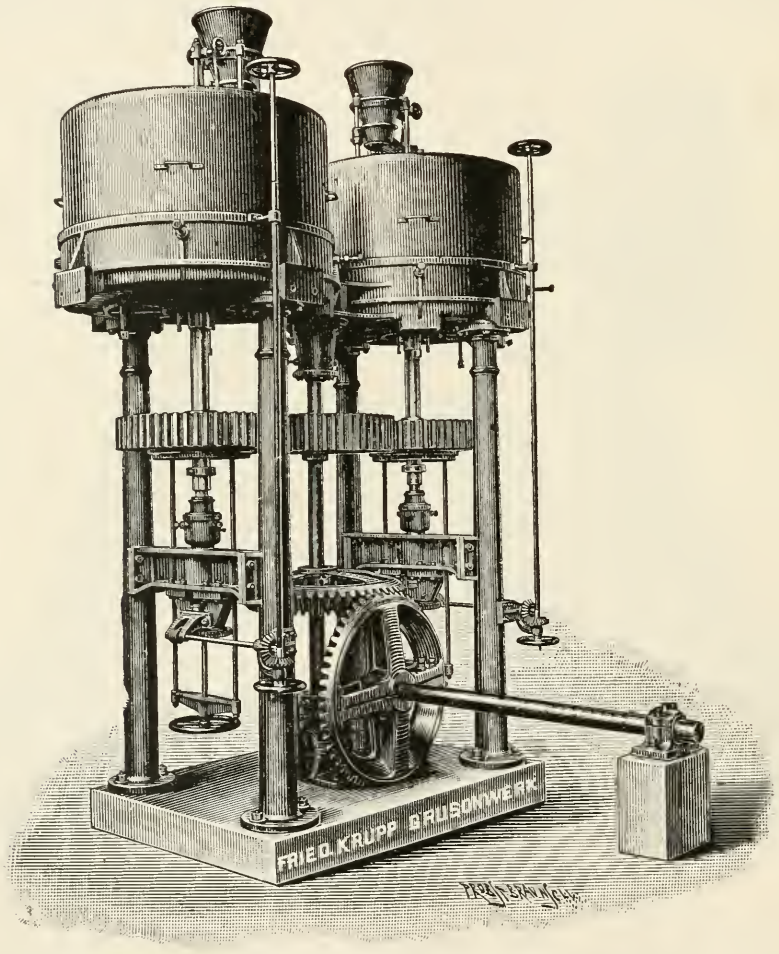


Fig. 2.—Flatstone Mill. (Lower stone dormant.)

done by means of an endless screw or by lever transmission with screw, and hand fly-wheel. The number of revolutions is 120 per minute for mills 5 feet in diameter, under which conditions a mill can grind about 5 tons of phosphate per hour, with 20 H.P. The mill is fed by a cup elevator and a shaking hopper, a single workman with an assistant can attend to two pairs of stones placed side by side. The mills of the same group are generally driven by

a single main shaft by direct cog-wheel gearing. Generally three pairs of stones are in use, two of which are at work and the other pair being faced. Fig. 2 shows two mills with the lower mill stationary arranged in a group driven with a common shaft by conical gearing.

Ball Mills.—The ball mill consists essentially of a rotary drum enclosed in a double cast-iron envelope and sieves. It contains a certain number of balls of different sizes. The inside face of the

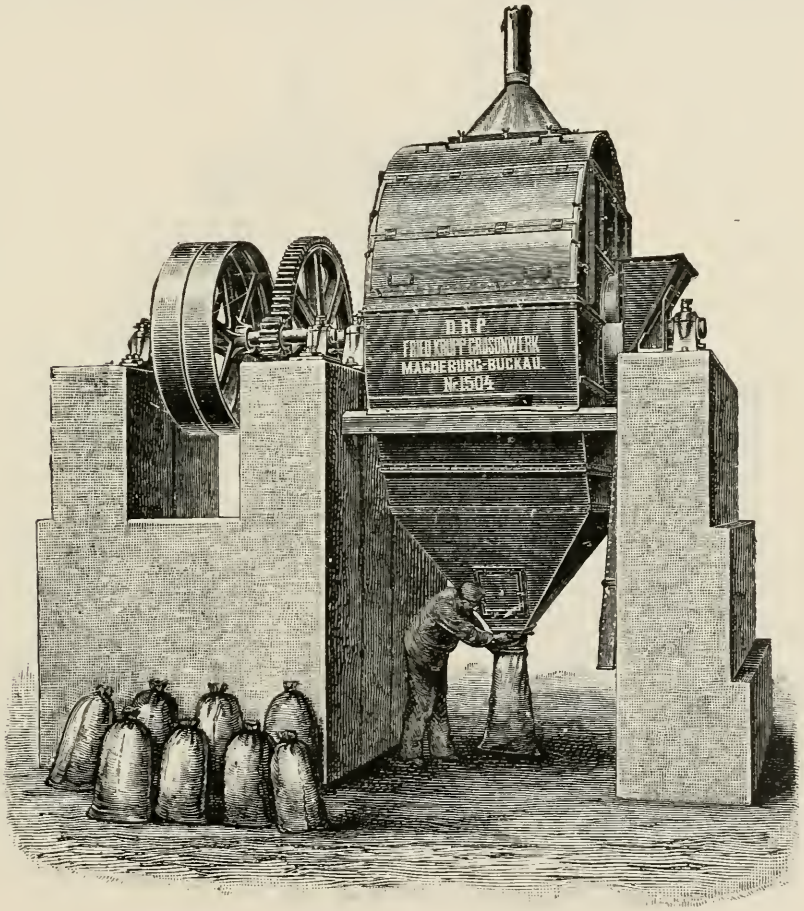


Fig. 3.—Ball Mill on Masonry Foundation.

bottom of the drum is lined with smooth plates of hardened cast-iron or of cast-steel. The circumference consists of triturated plates of cast-steel, and of such a shape that it creates a fall between two consecutive pieces. It follows that during revolution the balls fall from one plate to the other, and roll during the interval between two falls. Grinding is thus effected, by the shock of the balls and by crushing. The substance ground in the ball mills passes through holes in the triturating plates and falls on a first sieve, called the

protection sieve, which retains small fragments of material and only allows particles of a certain fineness to pass through. The fine grains then fall on a second sieve, which is the outside sieve, the wire gauze of which is selected according to the degree of fineness desired. The powder of the desired degree of fineness passes through this gauze and falls into the discharging funnel at the bottom of the machine, where it is bagged up. The cores from the two sieves are collected inside the mill by two openings arranged for the purpose, and again submitted to the action of the balls. The mill is fed

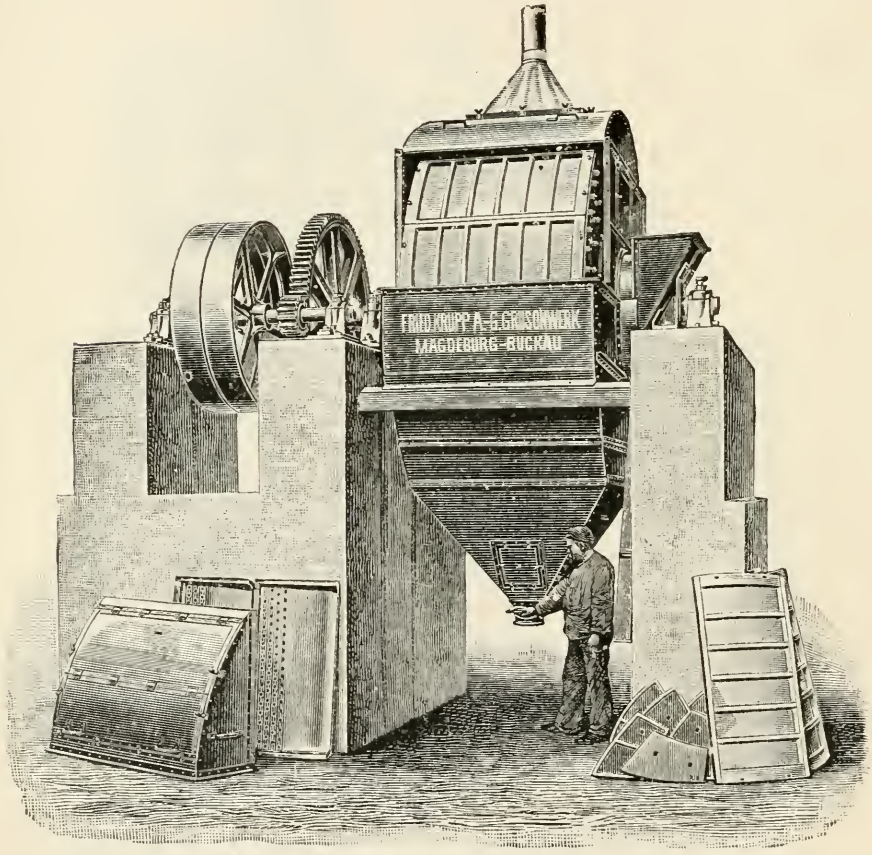


Fig. 4.—Ball Mill on Masonry Foundation—the Sieves exposed.

through a hopper fitted over one of the bosses, which has helicoid blades. During rotation of the mill these bring the lumps into the interior after the style of an endless screw. The wrought-iron cover is connected by a cloth jacket with a chimney which maintains the pressure of the air in the cover in equilibrium and evacuates the dust which is given off during grinding. The weight of the balls varies according to the nature and quality of the material to be ground. The mills in general use have a diameter of $6\frac{1}{2}$ feet and a section 39·3 inches. The charge of balls is 1 metric ton. These

naturally wear. It has been found that in grinding Florida phosphate forged steel balls lost 1 kg. (2·2 lb.) in a year working day and night whilst cast-iron balls lost 420 grms. (nearly 1 lb.: 0·924) in twenty-four hours. Their weight must thus be verified from time to time. To start the mill it is turned empty for half an hour to see whether the bearings heat. Then only is it charged with balls and phosphates. The drum ought always to be sufficiently full of material to be ground so that the falling balls produce a dull or

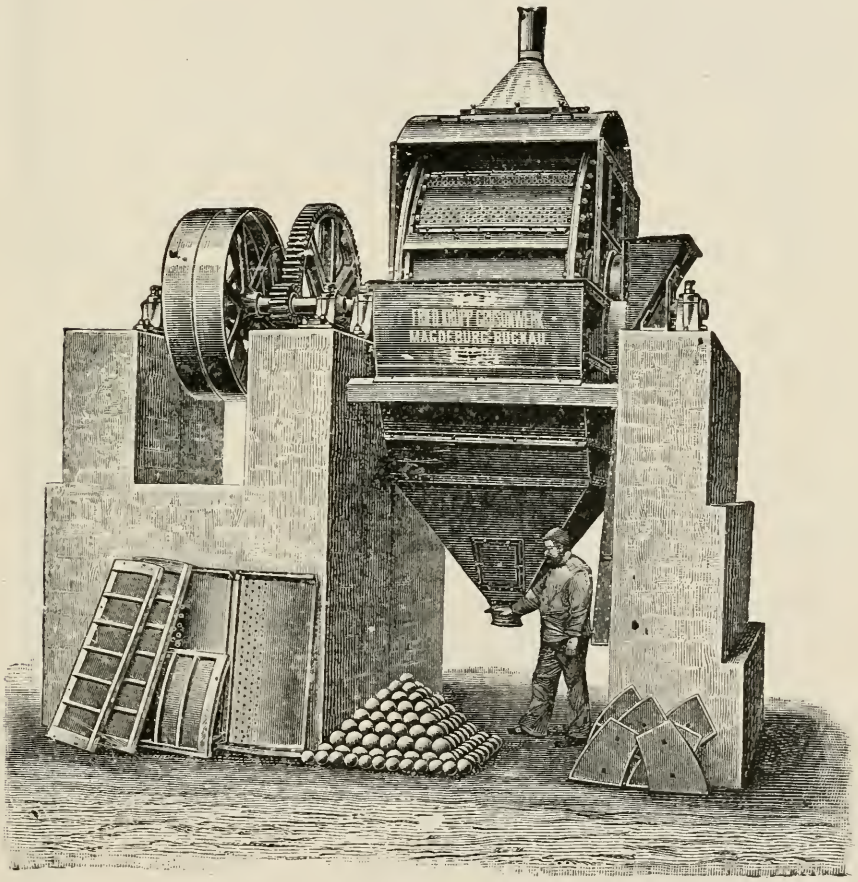


Fig. 5.—Ball Mill on Masonry Foundation—the Trituration Plates exposed.

deadened sound. Consequently, as soon as a bag of ground material is taken from the mill, it is fed with another through the hopper. When the mill has not sufficient feed its output is small and the workman is tempted to increase the load of balls, which has many drawbacks. The outside sieves are mounted on marked oak-frames, which prevent them being inverted, for they are not interchangeable. To stop up gaps or tears the simplest way is to glue pieces of calico above them with fish glue. During stoppages the inside of the

drum is carefully inspected, the screws of the frames tightened, and those of the manhole doors, because, in spite of the use of double

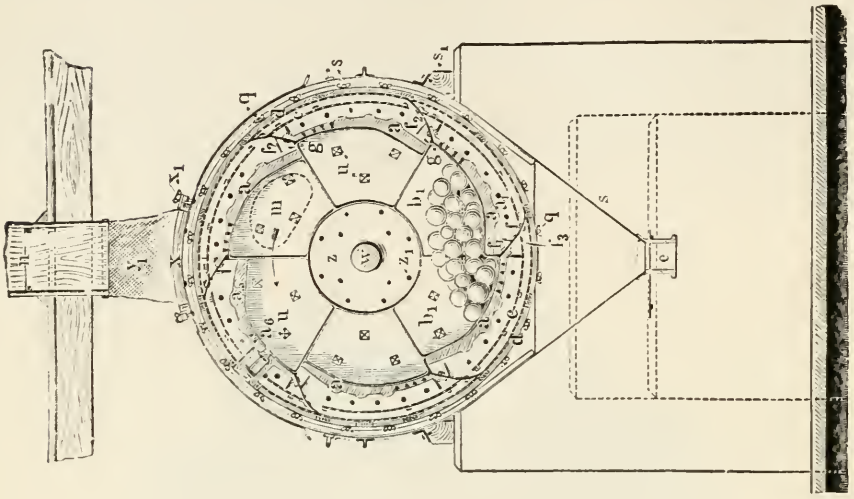


Fig. 7.—Ball Mill (cross section).

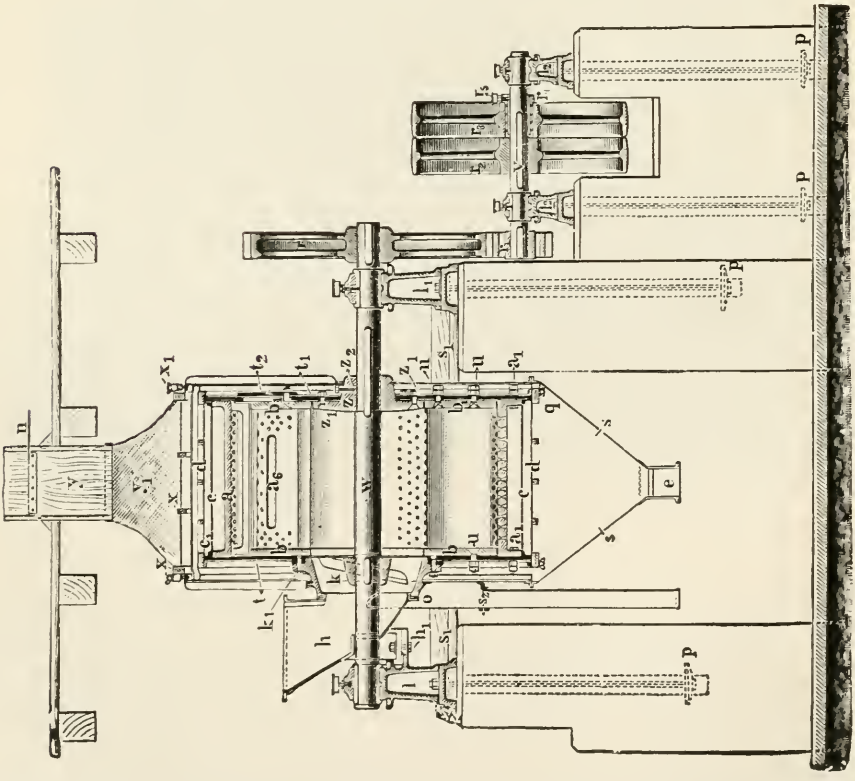


Fig. 6.—Ball Mill (longitudinal section).

screws, they are liable to become loose under the trituration to which they are exposed. Care must be taken to keep the sieves in perfect

condition. If the output of the mill decreases, the inside and outside of the sieves must be speedily cleaned. For that purpose the double envelope must be removed by a chain and counterpoise. In grinding wet phosphate the sieves get choked and they must be replaced by new at close intervals. It suffices in order that the phosphates can be rendered soluble that they pass through Nos. 60 to 80 mesh sieves, according to their origin and their nature. Thus Algerian phosphates and Carolina phosphates are passed through a No. 60, whilst coprolites, apatites, and Florida phosphates must pass through a 70 mesh sieve. Guanos and bone phosphates do not require to be ground so fine, owing to their capillarity, which lets the sulphuric acid penetrate easily into the interior of the granules. It suffices to pass them through a No. 50.

List of the separate pieces forming Krupp's Ball Mill.

a	Triturating perforated plates.
a^1	Collar screws.
a^5	Chimney plate.
a^6	Chimney cover.
b	Lateral plates (feed side).
b^1	Lateral plates (rear side).
u	Screws of lateral plates.
c	Coarse screen.
c^1	Screw of same.
d	Fine sieves (frame and cloth).
q	Screws of sieve frame.
e	Discharging funnel of dust cage.
f	Revolving blades.
f^1	Blade screws.
f^2	Protection screens.
f^3	Support of coarse screen.
g	Opening for the return of material.
h	Feed hopper.
h^1	Screw of hopper leg.
k	Feed and boss.
k^1	Screw of feed boss.
l	Column supporting hopper.
l^1	Rear column.
l^2	Gearing columns.
n	Damper.
p	Anchor plates.
r	Cog wheel.
r^1	Pinion.
r^2	Fixed pulley.
r^3	Loose pulley.
r^4	Case for same.
r^5	Lubricator.
s	Dust cage.
s^1	Wooden supports.
s^2	Collecting hopper and pipe.
t	Anterior lateral side.
t^1	Lateral posterior side with manhole m.
t^2	Manhole lid.
v	Cog wheel shaft.
w	Main shaft.
x	Frame work of dust cage.
x^1	Corner of the frame work.
y	Aeration chimney.
y^1	Coarse cloth union.
z	Rear boss.
z^1	Screw of boss.
z^2	Fixing screw.

As already mentioned, the ball mill is surmounted by a chimney. This ends in a dust chamber on the floor above; this chamber is itself provided with a ventilating pipe on the side opposite to that of the mill. When the chamber is not sufficiently well ventilated, the entrained steam condenses, the dust becomes wet, and the wood rots. It is, therefore, well to cover the sides with a coat of tar. In front of the chamber, that is to say on the spot where the dust collects, start two pipes closed by dampers, through which the dust falls into the grinding-room. It is, likewise, advisable to add a fan to the dust chamber, so as to renew the air in the grinding-

room. A greater quantity of dust then collects in the chamber, which then requires more frequent cleaning out. A fan making 200 revolutions suffices for two mills. A ball mill 6½ ft. requires 20 H.P.; it grinds 7½ tons of Florida phosphate, so as to pass through a 70 mesh sieve in twenty-four hours. It works continuously, and yields in a single operation a sifted and ground substance without other preparation than previous "cracking" up of the phosphate so as to reduce it to lumps the size of the fist.

In certain cases, especially in grinding basic slag, particles of iron may remain in the mill, which cannot be ground. They are removed through an opening made in the side which in normal work is closed by a lid which can be replaced by a discharge grating. The distance between the bars of this grating being inferior to the normal diameter of the balls, it suffices to give a few turns to the mill to evacuate the residual matter. In large-sized mills a manhole, fixed in one of the cheeks, enables the interior to be inspected. Ball mills have been the subject of many improvements. Those made by the firm of F. Krupp, Grussonwerk, Magdeburg, are of such solid construction as to stand any test and work for years without any repairs. The construction of this machine requires, in fact, a powerful equipment and select materials, conditions to which sixth-rate constructors can make no pretension.

Pfeiffer's Mill with Combined Air Separator.—This ball mill, amongst those just described, is the most interesting owing to its originality and its great working capacity. But its yield is perforce limited by the simultaneous sifting of the ground material; it gradually diminishes the fineness of the sieves, the surface of which is, moreover, too small compared with the work of the mill. Moreover, if the mill be overfed, the substance treated penetrates into the cavities of the sieve before being reduced to the desired fineness; the sifting is then retarded as well as the normal work of grinding. But affairs are radically altered if the powder be sifted separately. There is then no obstacle to the enlargement of this machine. This improvement has been effected by the firm of Pfeiffer Brothers of Kaiserlantern. By combining the ball mill with an air separator they have succeeded in creating a system of grinding remarkable for its great simplicity, and in increasing considerably the useful effect and output of the mills. The construction of the machine differs from that of the ball mill in the following details. The grinding-stages are comparatively small, each consists of a single piece of crucible cast-steel made with particular care, they have no slopes nor orifices of any kind to weaken them. Consequently they maintain their mechanical resistance to the last stage of wear and tear. There is no fear with this machine of the balls plugging the escape orifices, besides there is no need to enlarge these orifices by a rimer. The good construction of the

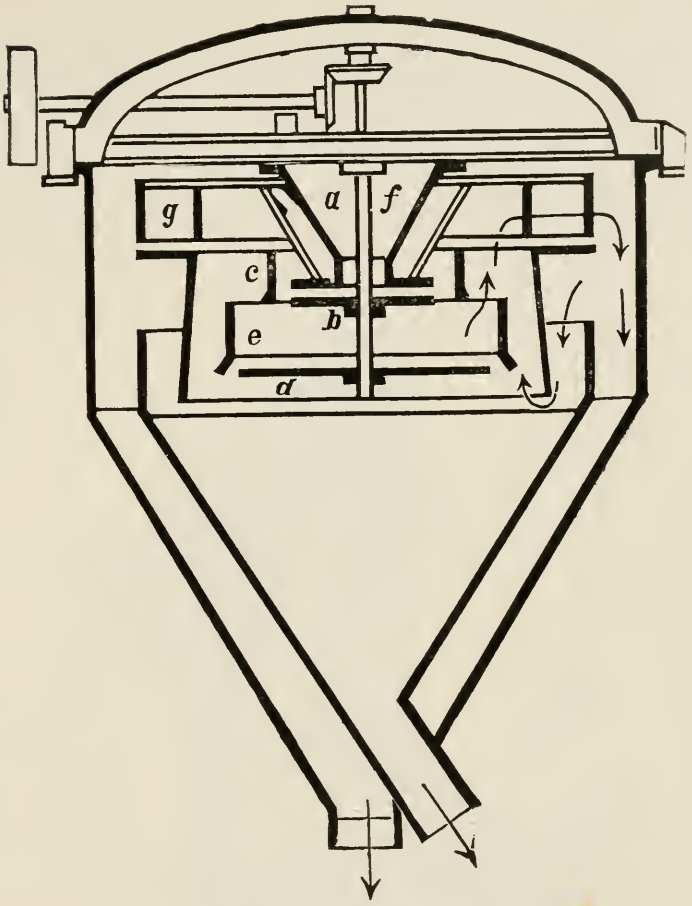


FIG. 8.—Pfeiffer Separator.

FIG. 9.—Pfeiffer's Separation Cone.

triturating plates and the quality of the metal used render them almost everlasting. The elevations (? incline) from one stage to another are fitted with orifices which allow the sufficiently ground material to escape. These orifices can be regulated from the out-

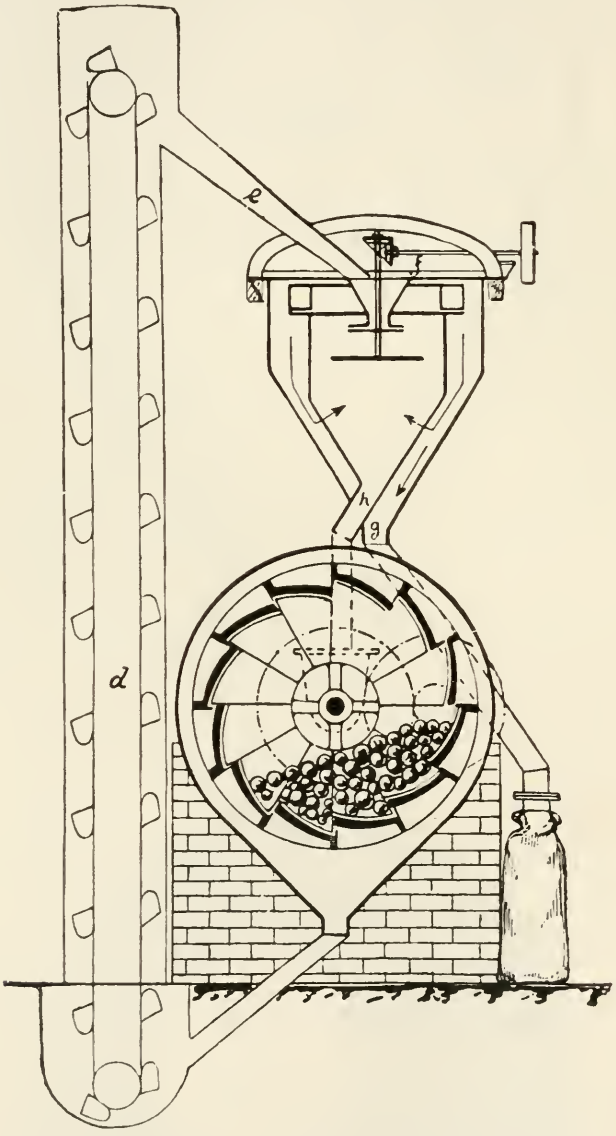


Fig. 10.—Section of Pfeiffer's Crusher-Separator.

side. They may be contracted or enlarged as required, so as to reduce the material to the required degree of fineness. As in ordinary ball mills, the wrought-iron cover which surrounds the drum ends in its lower part in a hopper; this collects the ground material and leads it to a cup elevator, which conveys it to an air

separator, generally placed above the mill. In this air separator, the fine flour is separated from the grains by means of a current of air produced in the machine itself and circulating there. The machine has only three orifices, the feed entrance, and the exits for the granular material, and for the flour. It requires neither sieve, dust chamber, nor auxiliary apparatus of any kind. The separator is shown in section in Fig. 10. The machine is constructed of wrought-steel, and consists of a cylindrical envelope with exterior cone and

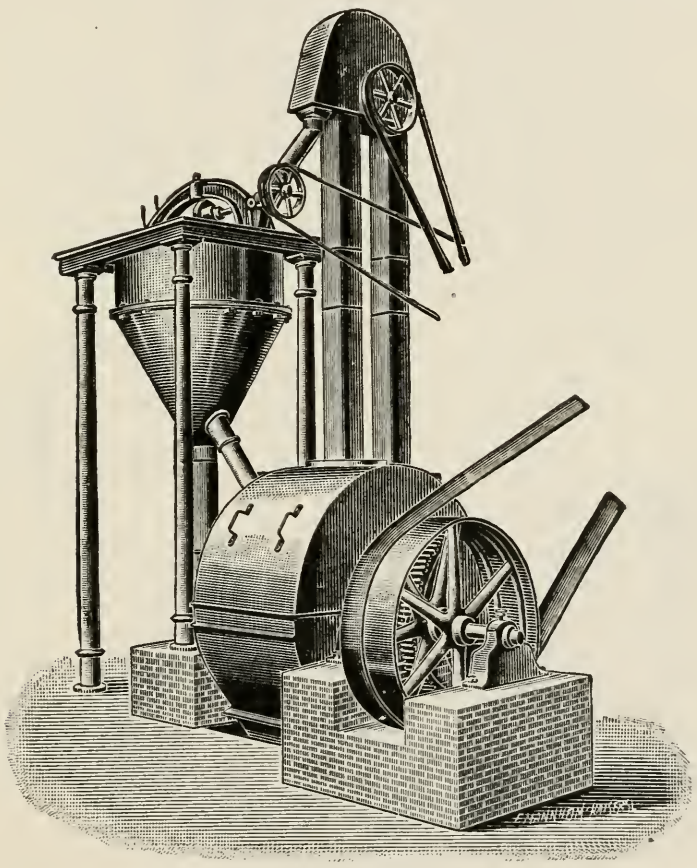


Fig. 11.—Perspective view of Pfeiffer's Crusher-Separator.

an interior cone arranged at a certain distance from the other. The ventilator *g* is driven by the shaft *f*. On the same shaft, below the ventilator, are two plates, *b* and *d*, which receive the material from the feed funnel *a*. In consequence of the rotation, the distributors *y* project the substance in all directions, and the current of air produced by the ventilator passes from below, upwards. The force of the current raises the fine particles and carries them in its train through the ventilator, and projects them against the exterior side, whence they fall into the *exterior* cone

and issue from the central aperture. The larger granules contained in the material which have traversed the current of air, without being carried away in its train, fall into the *interior* cone and issue by the lateral pipe, to repass into the mill if need be. The air returns naturally to the space below the distributor, so that the separator works constantly with the same amount of air, and so as to disengage no dust. The rods, with pins, to be seen on the cover of the separator, serve to raise or lower the annular obturator which regulates the degree of fineness of the substance. The force of the current of air diminishes in proportion as the obturator is raised. By these simple means, any degree of fineness can be secured. Once regulated, it works without interruption and supervision, and always gives a very uniform product. The ground phosphate can be bagged up directly or conveyed to silos, etc., whilst the granules return to the mill to be further ground.

Jaw-breaker Mills, Cracking Mills.—The jaw-breaker mill shown in Figs. 12 and 13 consists essentially of two jaws, *a* and A′,

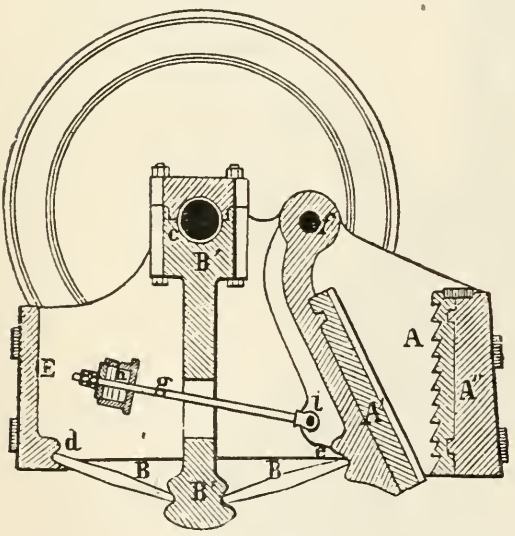


Fig. 12.—Jaw-breaker Crusher.

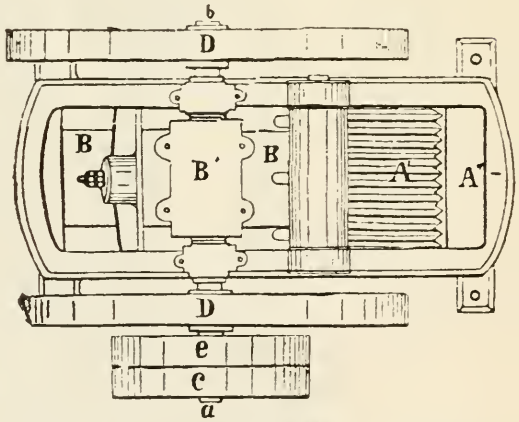


Fig. 13.—Jaw-breaker Mill (view from above).

of hardened cast-iron, dented or smooth. One of these jaws A″ is fixed on the anterior side of the framework, the other A′ is mobile and fixed on a jaw-holder which is animated by a to and fro motion round its axis *f*. This motion is transmitted by the excentric driving shaft *c*, through the intermediary of the excentric crank B′ and of a folding lever, formed by two hinge plates, BB, applied one on the framework in *d* and the other on *e* on the lower part of the movable jaw-holder. To avoid shocks the latter is joined in an elastic manner with the crank B, by means of the spring *g*. For each revolution of the shaft *c* the space A comprised between the fixed jaw-blade and the movable jaw is contracted, and its

minimum aperture determines the size of the crushed pieces. The angle of the aperture of the jaws is easily adjusted by a very simple

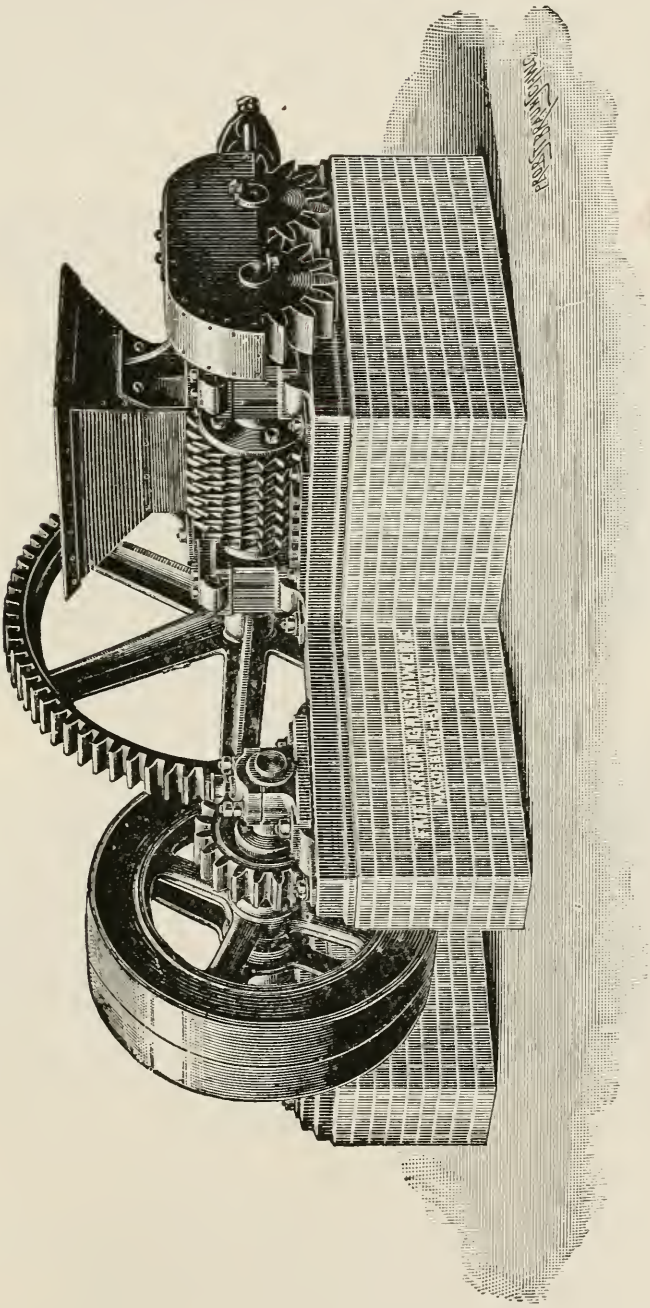


FIG. 14.—Toothed Roller Mill (belt-driven).

regulating arrangement, according to the nature of the material to be ground, and the degree of fineness required. The size of the pieces may vary from 2 to 7 cm. in section, with a proportion of

core, which depends on the degree of friability of the material. The hinged plates BB form safety pieces, they avoid all sudden shock, such as would be caused by the passage of a hard body, a piece of iron, for example, and then yield without any of the essential part of the machine being damaged. This mill is used for the preliminary crushing of rock phosphate, or phosphate in nodules of a certain size. It is fitted with two very powerful fly-wheels, which ensure regularity in working. A crusher of this

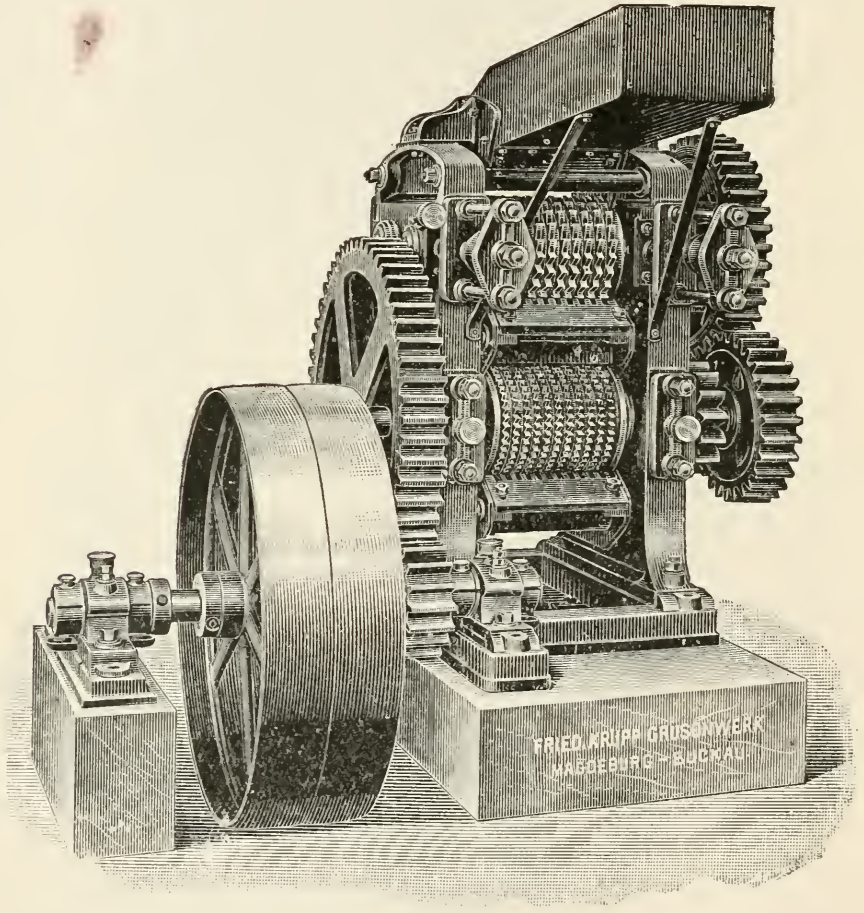


Fig. 15.—Double Roller Mill.

sort making 200 revolutions a minute can crush 5 tons of phosphate an hour with 3 H.P. Hand cracking, formerly in vogue, is now only adopted occasionally, when the quantity of phosphate in large lumps is not enough to warrant the use of the engine.

Toothed Roller Mills.—To crush green (raw) bones for fat extraction simple and double mills are used with toothed steel rollers. The rollers of the simple mill consist of a certain number of steel discs fitted with teeth, and of united intermediary rings in juxta-

position, in such a manner that the teeth of one of the rollers corresponds to the rings of the other. The discs resist any test and are readily replaced. The distance between the rollers can be regulated according to the size of the grain desired, by means of a regulating

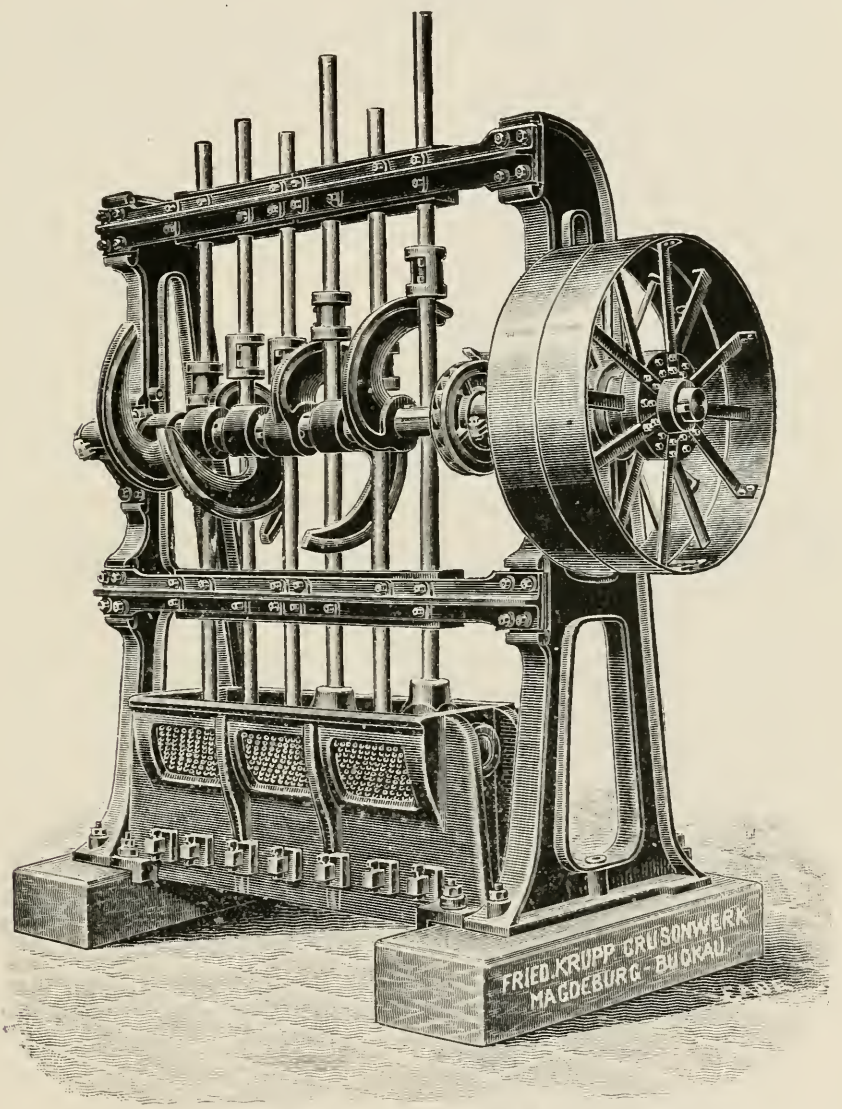


Fig. 16.—Stamping Mill.

screw fitted with a spring stud. This machine reduces the bones to the size of a nut, mixed with granules [? ½ inch bones], which are separated by sifting. The double mill comprises two pairs of rollers in a strong lateral framework. The upper pair is provided with big teeth and turns at a less speed than the lower pair, the teeth of which are finer. These double mills take bigger bones (whole ox

or horse heads) than the simple mills. They thus grind finer, which is an advantage in making gelatine, when it is desired to make as complete an extraction as possible and to obtain gelatine of good quality. The output of these machines is about 1½ tons of crushed bones per hour.

To grind degreased bones cast-iron stamping mills, fitted with a steel grate in the bottom, and on the longitudinal side with wrought-iron sieves, are used. The fineness of the holes in the grating and in the wrought-iron sieves depends on the fineness of grain desired. Stamping mills are of 1, 2, 3, 4, 6, 8 or 10 stamps of 1 cwt. to 2 cwt.; their yield per hour is about ½ ton of ½ inch bones.

Disintegrators—Mills with Percussion Blades Fitted in Circular Revolving Boss.—For grinding raw bones, dried meat, and blood,

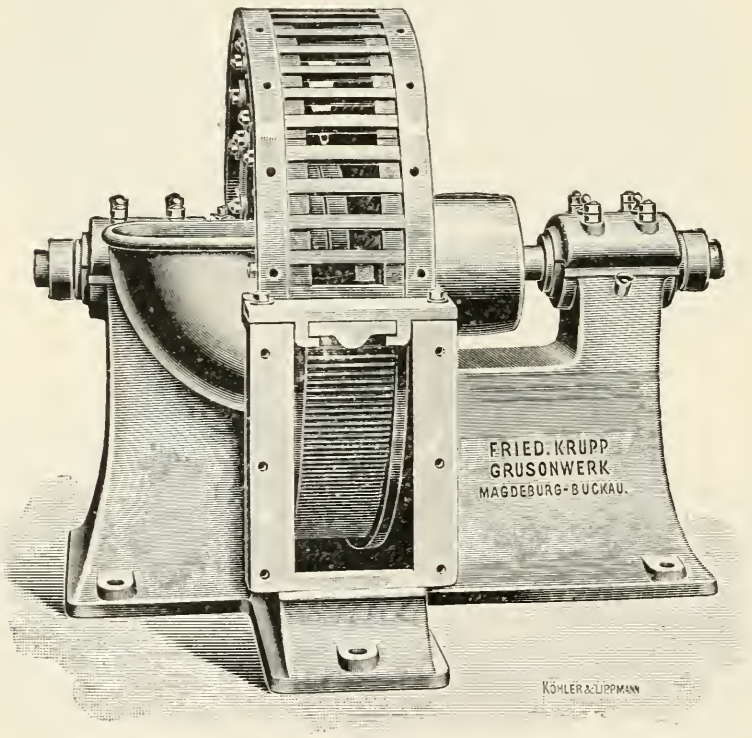


Fig. 17.—Disintegrator.

disintegrators are used with advantage. The mill consists essentially of a framework with vertical grinding cage, in which a boss fitted with blades revolves at great speed. The cage consists of two lateral sides and of a cover of wrought-iron, and a semicylindrical grate in two pieces, or completely cylindrical in four pieces. The lateral sides are lined inside with grooved plates of hardened cast-iron. According to the size of the mill the material to be ground may be in fragments of the size of an egg to that of the fist. When it is fed through the hopper it is seized by the blades and projected against the grinding plate and the steel bars; it thus

undergoes very energetic grinding; when it is reduced to the desired fineness it passes through the bars of the grate as a pulverulent product containing more or less core. For a width of $\frac{1}{8}$ of an inch the yield per hour is about 2 tons of degreased bones.[1] (See pp. 173 *et seq.*)

Elevators.—Cup elevators are generally used. Gall's wrought-iron chain and Ewart's chain deserve notice. These consist of small elements moving one within the other after the style of a hinge. Leather belts and rubber belts are only used exceptionally. The cups are of wrought-iron and furnished in the front with a steel armature; they are screwed on the elevator. Their dimensions vary with the size of the factory. Cup chains are generally fitted with a tight cover, enclosing the whole machine, and thus preventing the disengagement of dust in the factory. This cover comprises a cast-iron feed vessel with the top part of wrought-iron, and two square wrought-iron pipes carrying at their upper extremity a hood or coping of wrought-iron fitted with a discharge pipe; wooden feed vessels and covers may be made on the spot.

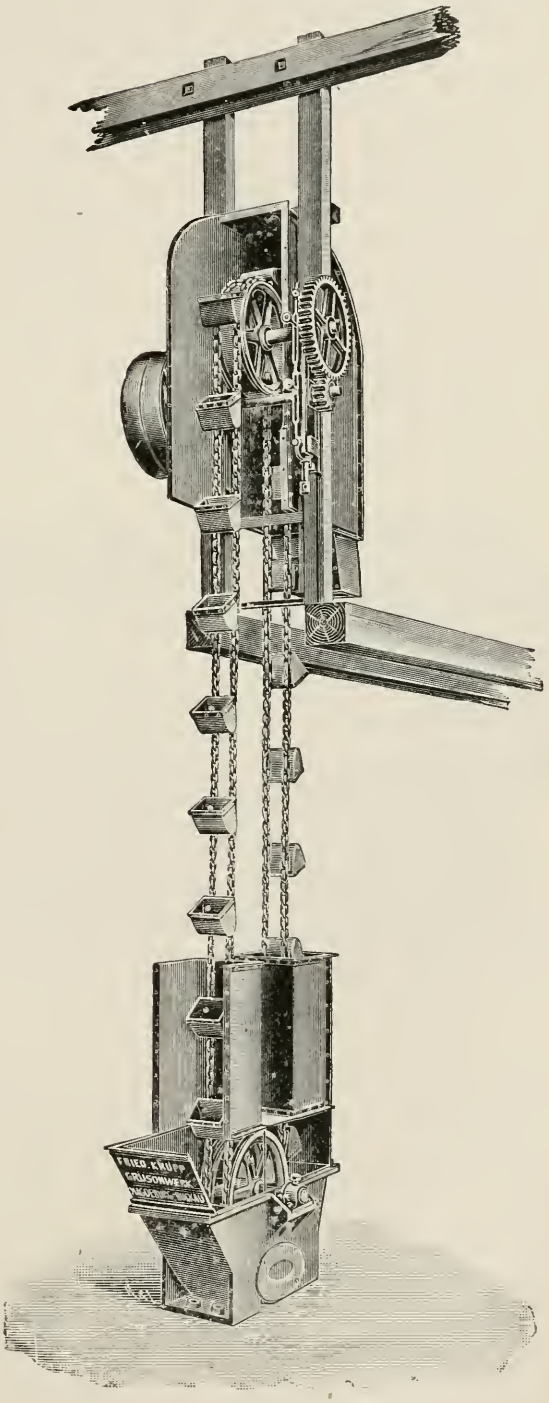


FIG. 18.—Cup-chain Elevator.

[1] This output abnormally high even for degreased bones through such a fine sieve, seems quite out of the question for raw bones. Bone grinding to such fineness is a tedious process. These machines, moreover, are like "short distance sprinters"—they soon fall out of gear, the belt comes off or breaks, the machine is blocked or the blades are smashed.—TR.

Sieves.—The sieves used in the chemical manure trade are of two kinds, viz. sorting sieves and sieves for fine flour. The sorting sieves are combined with the coarse crushers and serve to sort the crushed material; what passes through the sieve is taken to the mills to be reduced to a fine powder, whilst the core is returned to the crusher to be again crushed. Machines of this nature are conical or cylindrical. They consist essentially of an axis, which passes through their entire length, and carries iron stays, on which a perforated sheet-iron sieve, more rarely a metallic wire gauze sieve, is mounted, the meshes of which have a section varying with the nature of the material to be ground. They are fitted with a feed hopper and a discharge pipe.

The second class of sieves are more especially used for the sifting of the flour produced by the mills. They are also used to

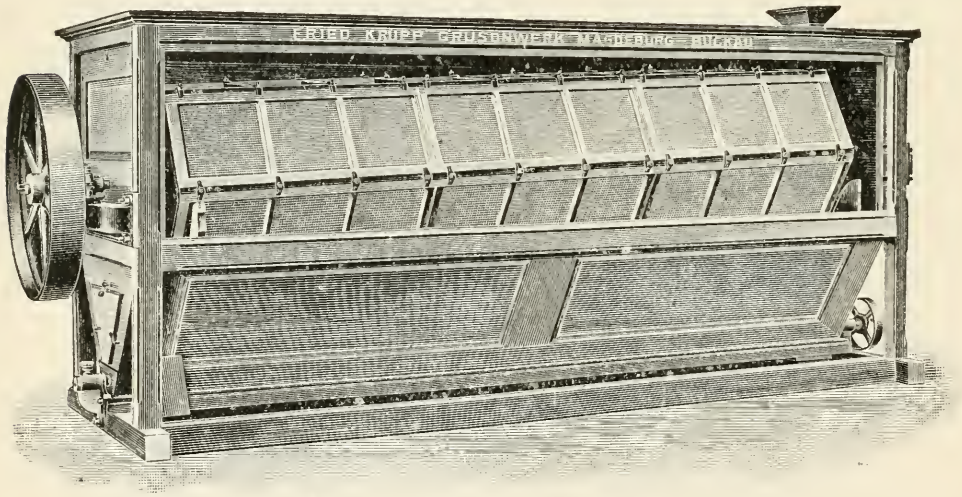


Fig. 19.—Sifting Machine (driven direct, enclosed in wood cover).

sort bone dust. The matter which passes through the sieve is bagged up, whilst the core is returned to the mills to be reduced to the desired fineness. As this material gives off much dust the sieve is generally covered in. Discharge pipes pass through the bottom of the cover. The construction of this machine varies according to the nature of the material treated—with substances easily sifted, the cylindrical form is used, whilst with substances which pass through difficultly, a hexagonal sieve fitted with a beater is used; the frames of the sieve are interchangeable and easy of access. Fig. 19 shows a sifting machine, driven direct, with wooden cover, constructed by Krupp. Besides these cylindrical sifters, shaking sieves are also used, comprising one or more flat sieves lodged inside a cover. The cover rests on springs or is suspended or driven by a crank shaft.

Filter Press.—The filter press is capable of interesting applications, not only in the manufacture of double superphosphates and precipitated phosphates, but also in the treatment of raw phosphates, in view of their enrichment each time that they have to be washed or mixed.

After mixing, the materials have a semi-fluid, non-pasty consistency. It is, therefore, necessary to separate the solids from the liquid mass in which they are suspended. The old decantation process gave good results. But it is easy to understand that the enormous quantity treated daily adapted itself badly to such an extremely slow process requiring numerous vessels and considerable space. In well-organized factories at the present day, a rapid decanter answers an urgent want. This rapid decanter is nothing more or less than the filter press, the yield of which is twenty times greater than that of the old process.

Under a small compass the filter press is, therefore, an apparatus presenting such a filtering surface that the solids and liquids are automatically and instantaneously separated. This apparatus consists essentially of a certain number of wood or metal plates separated by hollow frames, in which the solid matter aggregates as more or less compact cakes, whilst the liquid is pressed outside, passing through appropriate filter cloths.

The filter press is fed by a pump which propels the mud into the filtering chambers. The chambers are made tight by the pressure system of the filter and by the packing which the filter cloths give between the different plates when the latter are pressed in the centre. As regards the filtration of phosphatic material, manures, etc., the filter presses ought to exhibit such peculiarities of construction as to ensure the flow from the material without the formation of channels during the course of the operation. On the other hand, when the cakes are formed in the frames of the filter presses they still contain a certain amount of mother liquor. To obtain products as pure as possible these cakes must be washed thoroughly to purge them from the liquids which they contain. The filters should be so arranged that this operation of washing is thoroughly and absolutely effective. The "Etablissement des Filtre Philippe" of Paris, with whom the author has had business relations for more than twenty years, has specialized for many years in the construction of special filter presses for manures. Its make exhibits all guarantees for good working according to the nature and consistency of the products to be treated.[1]

Mixing of the Phosphate with Sulphuric Acid.—As already mentioned, the phosphate was formerly rendered soluble in pits, where the acid and phosphate were hand-mixed with suitable tools.

[1] The best duck (cotton) fabric will not stand superphosphate liquor a day. The writer found a woollen blanket to stand well.—Tr.

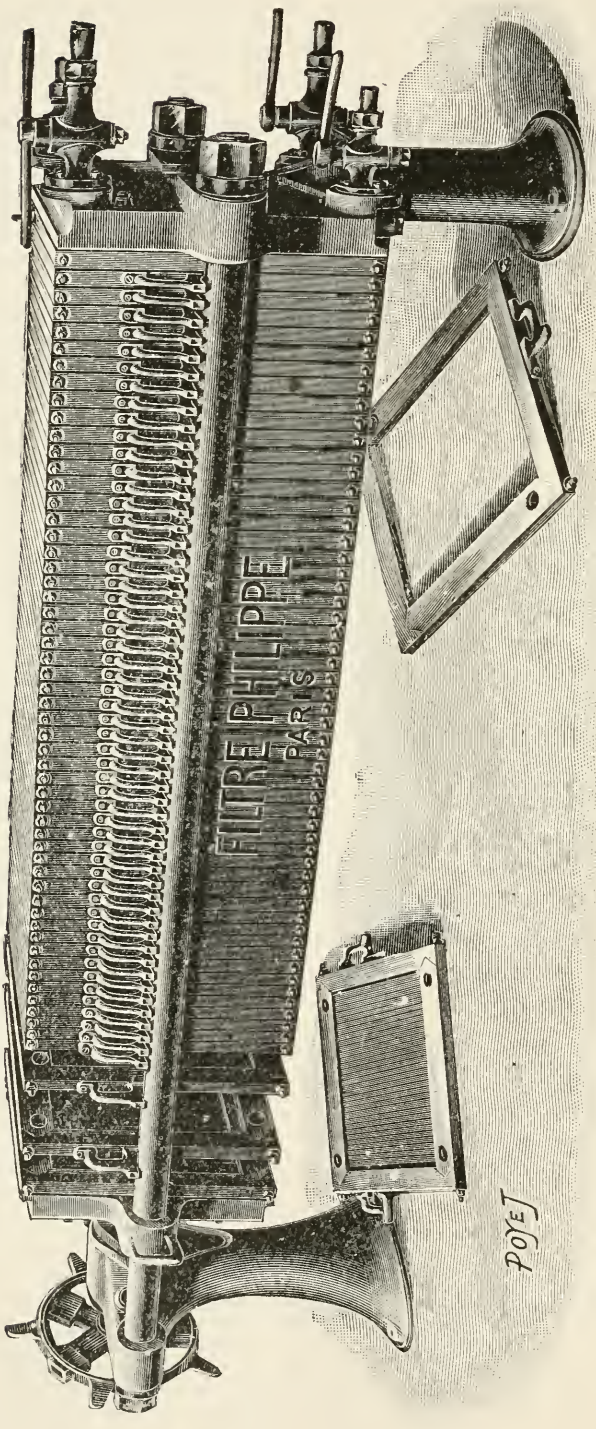


Fig. 20.—Filter Press.

In other words, they wrought like masons making mortar. But for thirty years this work has been done exclusively by mechanical means, which enables the work to be done more rapidly and in larger quantities at a time.

Consequently the mixing pit has been enlarged so much that in its new form it constitutes the chamber, or more familiarly the "den" or "house" in which the phosphate is rendered soluble. This chamber is closed, and care has to be taken to eliminate and render inoffensive the toxic gases which are disengaged from the material during its decomposition.

To mix the acid with the phosphate a "mixer" or mixing machine is used, constructed and installed thus: The mixer consists of an egg-shaped pan 1·6 metre wide at top (say 64 in.), and 1·20 metre (say 48 in.) wide at bottom, fitted with two discharge doors, with lever and counterpoise, which enables the mixing to be run into an enclosed space, called the decomposition chamber ("den" or "house"), which is built on the ground floor or sunk in the ground. In the pan a vertical shaft turns, driven by cog-wheel gearing, and carrying blades of a special form arranged in a helicoid manner;. these lift, throw down, and triturate the mass, after the style of a plough as it works the ground, and prevent it at the same time from being deposited and attached to the sides. It suffices to pull the bent levers to open the discharge doors, and thus let the liquid *a purée* fall into the decomposition chamber ("den" or "house").

The work is easy and rapid. The pan is made of cast-iron, with 2 per cent of a special alloy which renders it very resistant to acid. The arms of the agitator and the blades as well as the valves are of cast-steel. The mixing shaft makes sixty turns a minute; the mixing is triturated (churned) until the pulverized phosphate is intimately mixed with the acid. When the ground phosphate is too coarse to pass through a 70 mesh sieve the mixture remains longer in the liquid state, and then the length of time occupied in mixing must be prolonged. The acid, contained in a lead-lined tank, is drawn into a measuring tank by turning a valve; it flows through a $1\frac{3}{4}$ inch lead pipe into the mixer in the form of a shower of rain. At the same time the crushed phosphate—previously weighed and laid on sacks on two inclined planes to right and to left of the mixer—is run into the mixer. In certain factories the phosphate is brought to the mixer by an elevator, and received in buckets by means of which it is run into the mixer. The bags retain about 1 per cent of phosphate in the fabric. The mixer can take a charge of 225 to 250 kg. (495 to 550 lb.). When the phosphate is rich in carbonate of lime the mixture froths and threatens to prime. Such a mishap is obviated by diminishing the amount of phosphate. The acid and phosphate ought to be run in simultaneously and never after each

other. The mixer works continuously; no stop is made except in case of a breakdown. When one "mixing" is finished the sides of the mixer are rapidly dusted with a little phosphate to neutralize

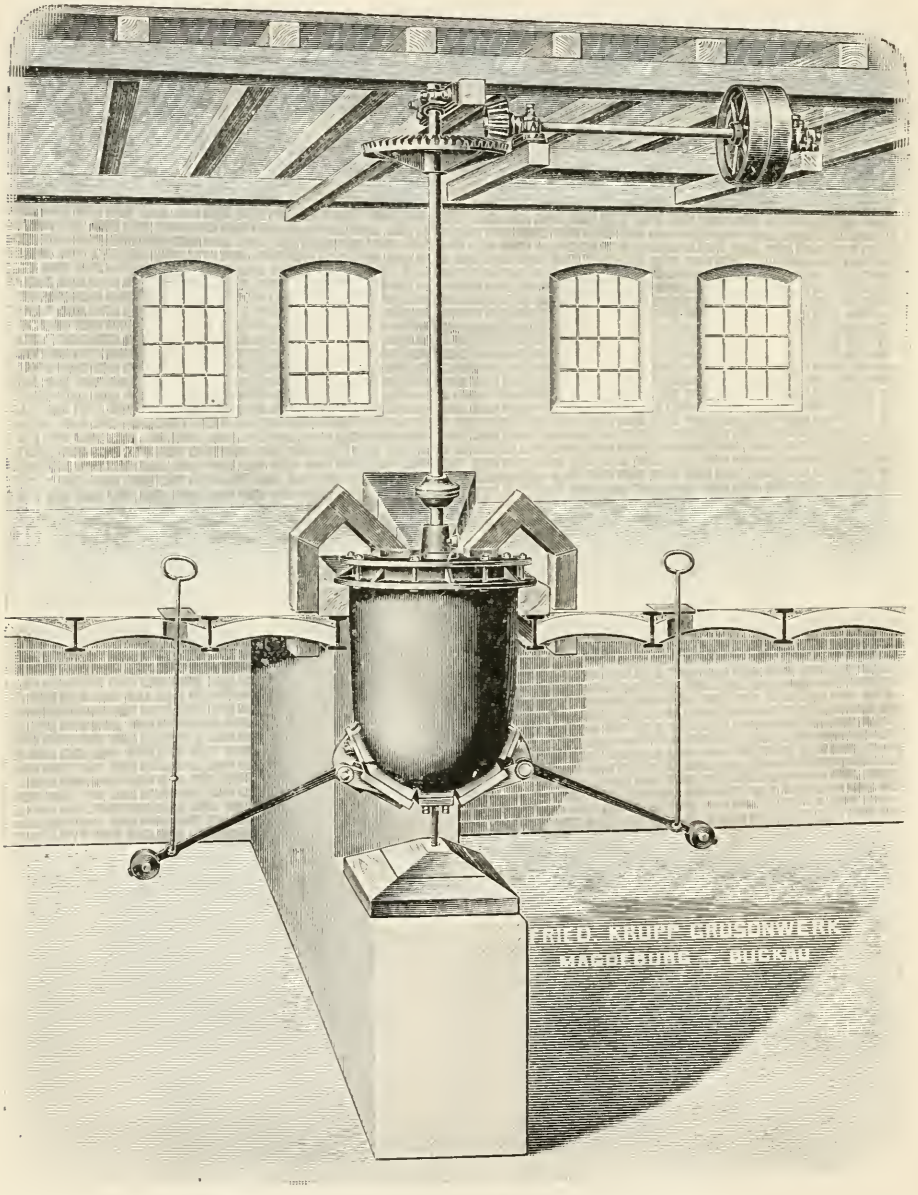


Fig. 21.—Mixer installed above the Superphosphate "Den".

any free acid left there which might corrode the metal. The working of the mixer requires three men; the first takes charge of the machine, the second superintends the measuring and running in of the acid, the third brings the sacks of phosphate. The charging of

the mixer lasts 1½ minutes; agitation takes two minutes, according to the nature of the phosphate; discharge takes half a minute. The "den" may be filled to ¾ of its height; the vacant space serves as a regulator for the evacuation of the gas. The decomposition of the phosphate by acid is effected not in the mixer, but principally in the "den" or "house". Cold acid is used, i.e. acid the temperature of which varies between 25° and 30° C. (77° to 86° F.), and of a density between 50° and 55° B. (106° to 123° Tw.). When the acid is at a lower temperature, the mixing does not heat enough to drive off the water, and yield a dry superphosphate. When the acid is too hot the mixing thickens too much in the mixer, in which case the acid may be further diluted.

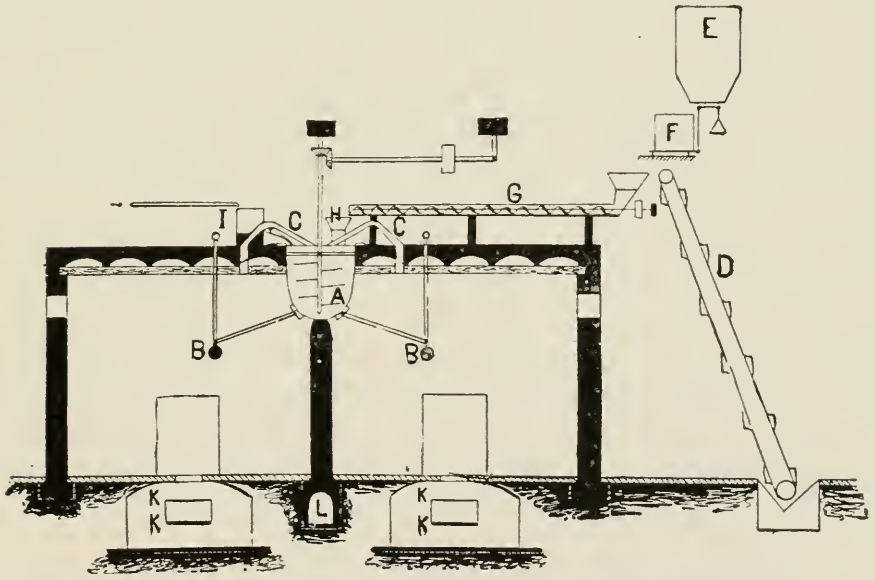


FIG. 22.—A. Mixer. B. Counterpoise. C. Gas Escape Pipe. D. Cup Elevator bringing the Raw Phosphate. E. Phosphate Reservoir. F. Balance for Weighing the Phosphate. G. Screw Conveyor. H. Feed Hopper. I. Acid Measuring Tank. KK. Underground Conveyor. L. Exit of Toxic Gases.

Owing to the gas given off, the thick liquid effervesces, and forms air-bells which rise to the surface; at the same time it heats up to 120° to 250° C. (248° to 302° F.). Gradually it settles in the "den," and after an hour it sets. An addition of dolomite carbonate of lime plus carbonate of magnesia keeps it liquid for some time longer, so that the water evaporated is then much greater.[1]

All the heat given off by the reaction ought to be utilized with that end in view (carrying off the water). It is only when this is

[1] A more valid reason for the greater dryness, if any, appears to be that magnesium sulphate crystallizes with seven molecules of water, and that is an efflorescent salt, not a deliquescent one. However, it is not usual to send a manure drier up the cups.—TR.

done that perfect solution is realized, and that a superphosphate that will behave well on subsequent manipulations is obtained. Of recent years attempts have been made to use hot sulphuric acid and inject hot air into the chamber, so as to render the phosphate perfectly soluble and to start the drying of the superphosphate, so as to simplify the final operations. But the results obtained were not satisfactory. The opinion of certain specialists may be endorsed. Such experiments will never be successful, because it is irrational to exceed a temperature of 100° C. (212° F.) in the "den" except in the case of phosphates of very good quality of which there is no need to fear retrogradation. It is better to leave the substance to itself during its chemical transformation and let it be settled by insensible gradations. Experience shows, moreover, that the injection of hot air into the mass gives it the consistency of mastic, and that the manure manufacturer always tries to avoid, knowing full well that the porosity of the superphosphate is the best condition to realize for subsequent operations. The construction of the decomposition house or "den" is not very complicated. The walls are two-brick thick; they are covered inside with a coating which resists acid. To consolidate them and prevent them yielding under the pressure of the mixing, they are fortified by iron T pieces, fixed to the base by masonry, and joined to the roof by cramping irons. The roof consists of iron T pieces, three feet apart, laid on the walls and connected together by iron rods or arches of masonry, the whole being covered by a coat of cement. All the ironwork is covered by paint to resist acid fumes. The house is fitted with a solid oak or pitch pine door consolidated inside by planks placed crosswise in the gutters. The chinks of the planks and the door are luted with a paste of clay so as to prevent air penetrating.[1]

In the early days of manure manufacture only one "house" was used, and the mixer was installed in the centre of the ceiling of the house; then two houses were installed with the mixer stride-legs between them; finally, later on, four houses have been built and the mixer placed at the crossing of the party walls. This plan gives excellent results. The mixer in that case is fitted with 4 discharge

[1] The great difficulty with the doors is that the acid eats away the bolts of any opening handle; the men must then perforce lever it open by the pick. The result is that where the pick is applied a chink is formed which gradually enlarges. But it is not a case of air *penetrating into the house*, but of fumes from the mixer or house *escaping* into the air through chinks. Both the district authority and the Local Government Board in Great Britain would at once proceed against any manufacturer letting the fumes *escape* into the air. If means be taken to prevent the *escape* of fumes, then it follows, *per contra*, that no air can gain access, because the pressure from within outwards is far greater than from without inwards. The air cannot penetrate until the gaseous fumes have condensed, and then the quality of the manure from that batch is fixed and determined. It is not advisable, however, to open the door too soon, unless in the case of hurried mixing specially. The doors are best of pitch pine.—Tr.

doors each of which empties into a house of its own. Each "den" has a capacity of 50 to 100 tons, according to the size of the factory.

Attempts have been made to find methods of rendering phosphate soluble more rapidly and more completely than by the processes actually used. To accomplish this the phosphate is reduced to a very fine state, i.e. to pass through a No. 100 sieve. A paste is made of it by drenching it with water or with acid of 10° to 20° B. and finally adding the rest of the acid at 60° B. But this process was soon abandoned, for the action was too violent and the metal of the mixer was attacked by the acid.

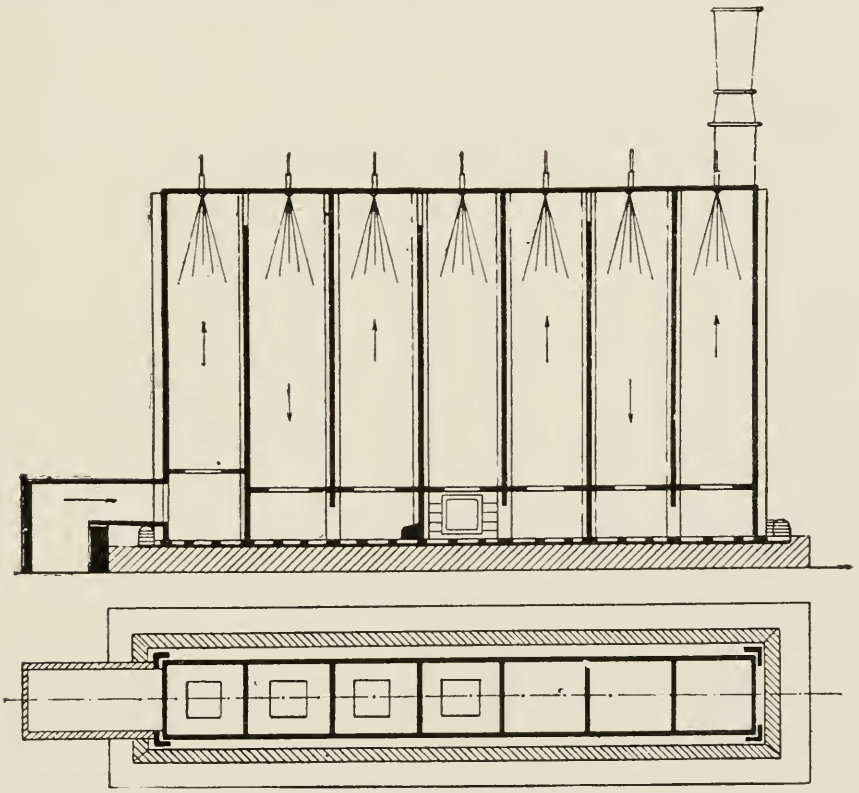


Fig. 23.—Toxic Gas Condensers (Benker and Hartmann's System).

Attempts have been made to render phosphates soluble by mixtures of hydrochloric and sulphuric acids without any great advantage. The superphosphate contained 0·30 per cent of hydrochloric acid which rotted the bags, besides the mixture of sulphuric acid and hydrochloric acid attacks the metal.

Evacuation of the Toxic Fumes.—The gases formed in the superphosphate "dens" cannot be allowed to escape into the atmosphere without being purified, in consequence of their bad smell and corrosive action. They are generally passed through a wash tower by means of a fan. Benker and Hartmann make very simple

installations and use for this purpose indestructible fans with washer purifiers which purify the gas completely. The fans should be rather powerful, so that the amount of air drawn into the "den" during discharge is sufficient to allow the labourers to empty the "den" under good conditions. Fig. 23 represents the tower constructed by F. Benker and E. Hartmann. It has several compartments and no packing. The gas penetrates into the first compartment, and ascending it meets a jet of water in the form of rain, produced by ebonite pulverisers (Kestner Lille). From the first compartment they pass into the second through the top, from the second they pass into the third through the bottom, and so on up to the seventh compartment, when they are exhausted. The silicic fluoride is decomposed by water into silica and hydrofluoric acid; the first can be separated by the filter press and the second can be concentrated to 12 to 15 per cent by volume and by mixing with alkaline chlorides, or even sulphates into the corresponding fluosilicates, which find a use in opaque glass manufacture and in flux enamelling.[1]

[1] The translator thinks it advisable to offer here a few criticisms on the method of making superphosphate as described by the author. First of all, the measuring tank has to discharge itself before it can be refilled, so the refilling cannot start before the phosphate is all in the mixer. However, it is just possible that it can be refilled in the two minutes taken up in continuing the mixing process, after all the acid and phosphate are run into the mixer—that is to say if no hitch occurs. But if the same principle were adopted, with 2 to 2½ ton mixers, as used in Great Britain, and the agitation prolonged, in accordance with the weight of the mixing, then a 5 cwt. mixing taking two minutes' agitation, a 50 cwt. mixing ought to take twenty minutes, whereas it is shot into the "den" shortly after the last bag is up the cups and the last drop of acid run in. When the mixer is hand-fed and the lid removed, the fumes escape into the air of the building, and that is bad for the men at work. Again, a cast-iron mixer is a dead-weight on the boundary wall between the two "dens," and these eaten away by acid are none too strong. Again, in Fig. 22 the phosphate should all be weighed before it is shot at the foot of the cups, and the elevator should then discharge right into the mixer, and the spray of acid and the spray of phosphate should meet at the same spot. Then with a horizontal instead of a vertical mixer a wooden tank lined with 5 lb. lead can be used. The only cost is the mixing shaft and blades and the gun-metal discharge sluice valves. With such a mixer, to take 2½ tons of superphosphate, the mixing shaft is best made in two pieces, and the middle extremities ending in projecting studs turned in a lathe are screwed up with bolts and nuts. Then if one-half of the shaft break, the other part can remain *in situ*, and the whole shaft need not be recast. But care must be taken that the two halves revolve in perfect symmetry. Again, it is a very awkward thing to empty a vertical mixer when it sets. All that has to be done with a horizontal lead-lined mixer is to remove the (loose) boards by which it is covered and set a man at work to dig it out, and if the mixer is near the eaves all that he has to do is to remove a tile or two to secure ventilation. But in a vertical mixer, were it not for the tiny mixings described by the author, it must be a more than ordinary trying task. Coming now to hot acid versus cold acid: some phosphate can be mixed very well with acid, e.g. Carolina phosphate. But Somme phosphate requires hot acid, and the translator found it advantageous to keep a 10 ton tank at 140° F. This he diluted with water as mixed as the author suggests. Somme is not in any way the *beau ideal* of a raw material.—Tr.

CHAPTER VII.

CRUSHING, SIFTING, DRYING, AND STORING OF SUPERPHOSPHATE. RETROGRADATION.

Emptying and Shifting the Superphosphate House or "Den".— Emptying the superphosphate "den" is still done in a primitive manner, which consists in charging the superphosphate with the shovel into the receiving vessel of an elevator or into half-ton wagons.[1] The latter are run towards a crane that lifts them and spreads their contents over the heap from a certain height. In default of the elevator the heap could not be raised high enough and more capacious warehouses would be required.

Another method of shifting the superphosphate out of the houses, consists in emptying them from below. In that case the house is built over a sort of cellar, in which the material drops on to an endless belt 20 in. wide, through holes in the floor covered by iron lids. The belt drops the superphosphate on an inclined plane ending in the receiver of an elevator, which discharges the superphosphate either on the heap or into a Carr's disintegrator, or into a jigger, according to the method of working adopted. The best plan is to give the elevator a certain slope and use comparatively large cups, because fresh superphosphate ought to be pressed as little as possible, otherwise it is converted into a gluey mass difficult to manipulate and to dry. The emptying of the superphosphate "den" is not exactly a pleasant job, even if the heat and the gases, still persistent there and disengaged when the superphosphate is displaced, be not taken into account. The workmen are therefore obliged to work with aspirators, the sponge of which they should keep moist, so as to prevent any accident. The superphosphate ought to be extracted from the chamber whilst it is still hot, so that the vapour may be eliminated and not condense by cooling. If the superphosphate

[1] But in working even on a fairly large scale, in Great Britain the work of shifting is sometimes still done by barrow, plank, and gang sack. One man "gets" the stuff with the pick, two men fill the barrow, a fourth or fifth man, if need be, wheels it on the ground at first, then up a plank, and when the plank is too steep the barrow men cease to ply their barrows and take to gang sacks, their heads and shoulders being protected by a "backing" cap or at a pinch by a sack.—Tr.

has been well made it soon crumbles when exposed to the air; if badly made it forms lumps which do not crumble in the air, and the outside of which is damp from free phosphoric acid, whilst the inside forms any nucleus of neutral phosphate of lime: this occurs when too strong acid has been used. The core, sifted from the material, is dried in an oven if it cannot be crushed in a Carr's disintegrator.

In a general manner the reaction which superphosphate undergoes during the process of being rendered soluble, and which consists in the precipitation of sulphate of lime and its conversion into crystallized gypsum, is accomplished rapidly. Certain phosphates, however, form exceptions to this rule: crystallization is stimulated

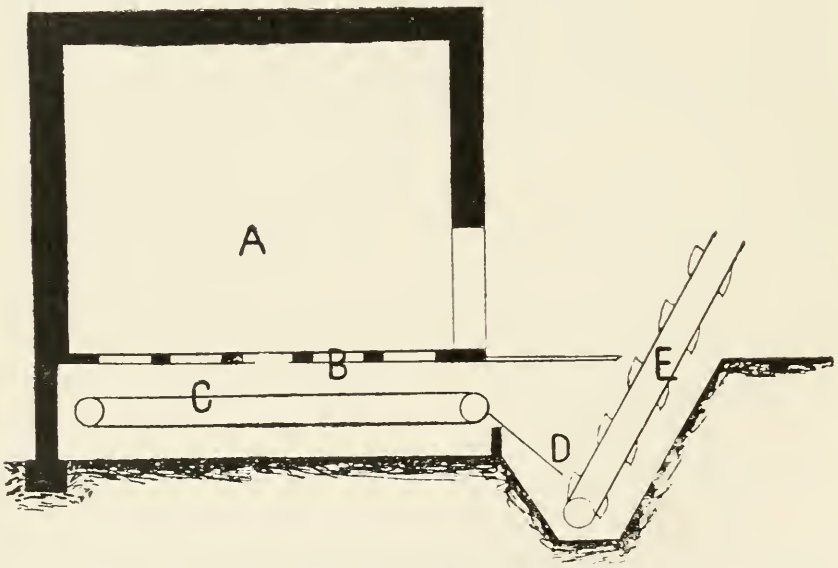


Fig. 24.— A. Superphosphate Den. B. Discharge Apertures. C. Belt Conveyor. D. Elevator Receiver. E. Elevator.

by stirring them with the shovel and the process finished by drying.

New Methods for the Mechanical Extraction of Superphosphate from the "Den".—The manipulation of superphosphate being dangerous, on account of the toxic gases which are disengaged, efforts have been made to empty the houses mechanically. But the appliances used are costly and defective, especially owing to the false position at the door of the excavation plant. Benker and Hartmann's mechanical extractor suppresses these drawbacks, in so far that the excavating organ is arranged so as to support its shaft at its two ends. Figs. 25-28 show the arrangement which forms the subject of their invention. Fig. 25 is a longitudinal section. Fig. 26 is an end view. Fig. 27 is a plan. Fig. 28 is a detail.

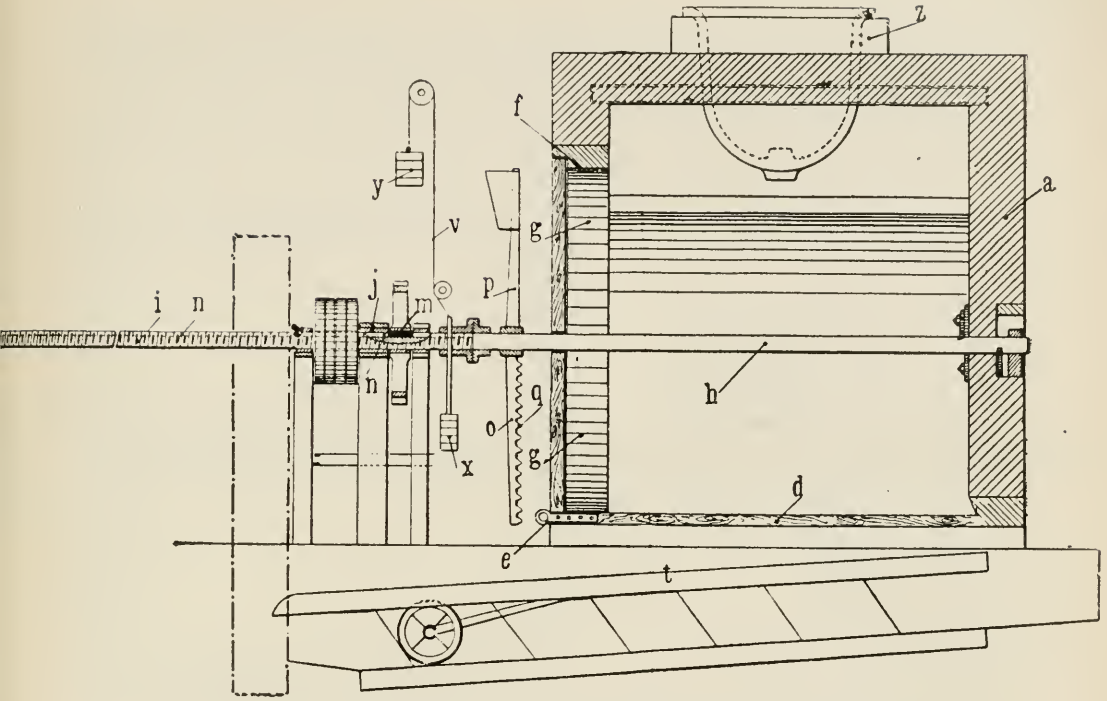


FIG. 25.—Benker and Hartmann's Mechanical Remover of Superphosphate from " Den " (longitudinal section).

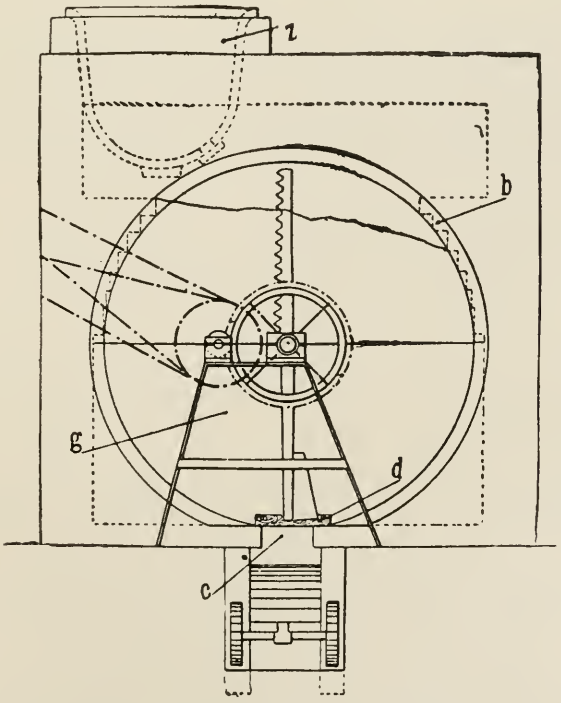


FIG. 26.—Benker and Hartmann's Mechanical Remover of Superphosphate from " Den " (end view).

The superphosphate " den " *a* has interior lateral sides *b* arranged in grades, reversed above, in such a way as to give to the final block a form approaching that of a cylinder. The floor of the " den " is pierced in its centre by a longitudinal opening *c* covered by a wooden trap *d*, one of the ends of which is fitted with a ring handle

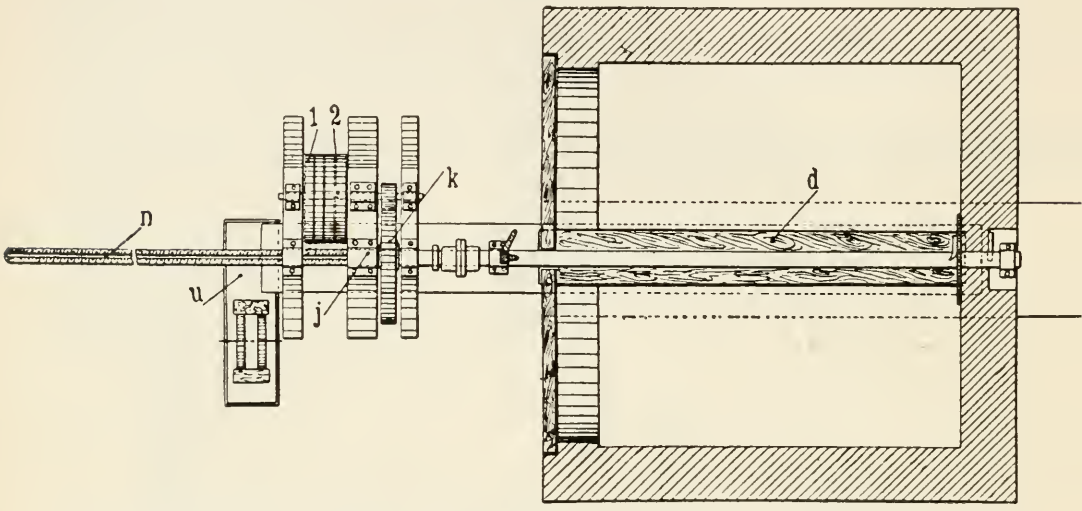


Fig. 27.—Benker and Hartmann's Mechanical Remover of Superphosphate from " Den " (plan).

e. The " den " has in its face a circular opening *f* shut by a door *g* in two parts. This " den " is traversed through its whole length by a shaft *h*, supported on two suitable bearings so as to dovetail into and continue a screw shaft *i* mounted in a fixed screw *j*. A cog-wheel *k*, geared to the outside screw part of the shaft *i*, has a claw

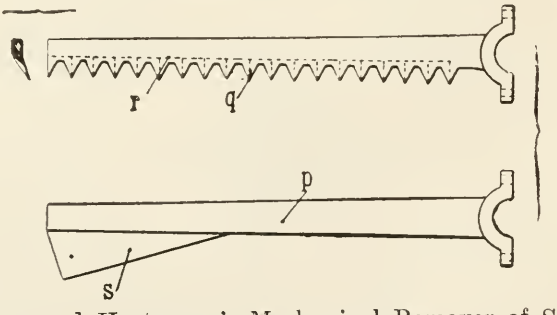


Fig. 28.—Benker and Hartmann's Mechanical Remover of Superphosphate from " Den " (detail).

m, which penetrates into a longitudinal gutter *n* of that shaft, so as to connect the shaft *i* with the wheel *k* in the direction of rotation, but letting it glide freely. On the shaft *h* two arms *o* and *p* are fixed diametrically opposite one another, one of which *o* forms a sort of compound knife, fitted with teeth *q* projecting from the

blades *r*. The other arm *p*, conveniently fixed behind the first, is fitted at its free end with a sort of shovel or spoon *s*. A conveyor *t*, of known construction, is arranged below the opening *c* of the den and empties into a suitable elevator *u*. A band of stuff *v*, fitted with suitable counterpoises *x* and *y*, is arranged above the screw shaft *i*, so as to cover it when it enters inside the den. A mixer *z* is fixed at the top of the "den," and the installation may be completed with fans and condensers of any desired construction. The cog-wheel *k* may be driven by any suitable means, for example by a play of pulleys fixed and movable, 1 and 2 acting in different directions. The working is as follows: During the mixing of the mass of superphosphate the trap door *d* covers the opening *c* and the door *g* covers the circular opening in the front of the "den," the two arms, *o* and *p*, being kept outside the "den". After the superphosphate has set, the trap door *d* is withdrawn by aid of a hand-winch, not shown on the drawings, then the door *g* is removed. The whole of the shafts, *h* and *i*, are caused to revolve in a suitable direction to bring the mechanism inside the "den". When the teeth *q* of the arms *o* come in contact with the mass of superphosphate, it penetrates into the interior of the mass, detaching ribbons which break, forming small fragments, which fall to the bottom of "den". The blades *r* in turn come in contact with the portion of the matter projecting between the teeth, detach these likewise in the form of ribbons, which collect at the bottom of the "den". The shovel *s* at the aperture C brings these fragments, from where they fall into the conveyor *t*. Whilst the shaft *i* is penetrating inside the "den," the cloth *v* unrolls and covers this shaft so as to prevent it being crushed by lumps of superphosphate. When all the matter in the "den" has been reduced to fragments and evacuated by the conveyor the rotation of the shafts *h* and *i* are reversed, until the arms *o*, *p* are outside the "den"; the sliding door *d* is replaced as well as the door *g*, and the mixing of a fresh batch started. This arrangement is simple and economical. The arms supporting the cutting knife is fixed on a shaft supported at both ends, which prevents all work in false directions and secures a better output. The attack of the material by a vertical knife facilitates the conveyance of the fragments it turns out. This arrangement may be applied to all existing "dens" by modifying or not the inside shape of these "dens," so as to render them cylindrical. During the mixing of the superphosphate no delicate piece of the mechanism comes in contact with the material, so that the mechanism is practically unwearable and little liable to damage. The screw shaft may be replaced by any other arrangement giving to the arms *o*, *p* a forward helicoidal motion, and fitting the whole mechanism with an arrangement allowing the speed of the displacement of the arms to be increased at will; for example, for their return. The invention applies to the

extraction of superphosphate as well as to manures, or analogous chemical products. Summing up, the inventors claim :—

(1) An arrangement for the mechanical shifting of superphosphate consisting of a vertical shaft *o*, mounted on a horizontal axis *h*, and driven with a simultaneous movement of rotation and translation of which the blade *r* comprises projecting teeth *q*, preferably incurved on the axis, with the object of first of all bringing the teeth in contact with the material so as to commence the attack of the material by the teeth, and finish it by the blade.

(2) A method of applying the arrangement described in (1), in which the horizontal shaft *h* of the knife, comprising a radial arm *p*, fitted with a shovel *s*, is supported at its two extremities and forms part of a screw shaft *i*, engaging into a fixed screw *j*, and gearing with a driving cog-wheel *k*, in which it can glide so as to avoid any false working.

Allegri's Plant for Shifting Superphosphate from the "Dens".— Allegri, the engineer of the united factories of the Italian agriculturists, has also patented a machine to replace manual labour in shifting superphosphate from the mixing "dens". His appliance consists essentially of a sort of plough, to which a horizontal and vertical motion is imparted. This plough traverses the chamber in the direction of its length, and at each passage it detaches a small slice of superphosphate and discharges it through the door in the top of the chamber into a conveyor of some sort. A single workman can overlook several of these machines. This machine shifts 10 tons of superphosphate an hour. The force necessary is 4 H.P. The cost of upkeep is limited to changing the plough from time to time, which is the only part exposed to contact with the superphosphate. The appliance may be fitted to any existing "den" with a few alterations.

Another method of shifting superphosphate "dens" is comprised in British patent No. 20,446 (25 Feb., 1907). It consists in shifting the superphosphate by a movable platform, on which it rests so as to expose sides and top, so that the mass can be broken up in the open air. With this end in view the floor of the decomposing "den" is mounted on wheels; in this way it may be drawn out of the "den" by appropriate mechanism through a movable door made in one of its sides. The superphosphate shifted out of the "dens" is then broken up by any mechanical arrangement and charged into conveyors to be conducted to the drying machine. Finally, the following arrangement of the superphosphate "dens," in a Bordeaux factory, is described, as an interesting improvement. The new "dens" consist of long channels in a mass of masonry work below the mixer. These channels are 1·6 to 1·8 metres above the floor of the factory. A metallic cradle placed inside these channels, of which it assumes the form (naturally !), is propelled by a winch

fixed on the floor on the side opposite the discharge. During mixing the superphosphate as it comes from the mixer adheres as an immense cake to the bars of the cradle. To shift it, it suffices by means of the winch to bring the cradle out of the den, where the product is collected in trucks. The workmen have only to detach what adheres to the bars and to let it fall into the trucks, by means of rather long tools, so as to keep at a suitable distance. A hood connected with a fan is placed on the discharge door, so that the fumes are drawn from the exit of the "dens" and cannot inconvenience the workmen. The superphosphate is then conveyed by wagons into the Persian wheels which elevate it into the drying ovens. A fan draws vapour and dust from the dryers, and propels the first into a condensation tower and the second into a dust chamber. The manufacture of superphosphate, owing to these new arrangements, presents no serious drawbacks as regards the health of the workmen or of the neighbourhood.

Breaking up and Sifting or Screening of Superphosphate.— The superphosphate placed in a heap in the fresh state consolidates itself so much that it has to be broken down or "got" by the pick and shovel. In order to get it to a proper degree of fineness, it was formerly projected against an inclined sieve (screen) and the "core" crushed with the back of the shovel. This sieve, of 6-8 mm. in section, that is a quarter inch sieve, is still in use in small factories.[1] Shaking and regulating sieves are also in use. To get the superphosphate from the heap, the best plan is to attack it at the tail corner by drawing it towards oneself with the pick. By lifting it in successive layers it would run the risk of being compressed. Care is taken not to excavate underneath when the heap is more than 6 ft. high.[2]

Compact superphosphate is reduced to a pulverulent state by Carr's disintegrator or a crusher fitted with steel teeth.

Carr's Disintegrator.— This disintegrator was invented by Thomas Carr of Montepelier, near Bristol, and patented in Great Britain. It consists essentially of two, four, six, or eight concentric cages, the cylindrical sides of which consist of metallic bars *b*,

[1] Well-made superphosphate does not require to be put through quite so fine a screen as a one-fourth inch screen except for the dry mixing of compound manures. Good made superphosphate passed through an inch screen is fine enough for most purposes, and through half an inch for all purposes, and the price is now cut so fine that to add to the cost by passing it through a needlessly close sieve is irrational, the more so as superphosphate, as distinguished from wet mixed compound manures, has little or no core. It only wants a touch with the shovel to break it up to fine powder.—Tr.

[2] But that is exactly what the man who gets the manure with the pick does. He knows the right time to stand clear, and only the undermined portion falls, and that quite gradually and without undue precipitation.—Tr.

encased on one side in plain discs *a*, on the other on crowns *a*. The first (inside), third and fifth cages form an aggregate of a single piece, screwed with the boss of the disc on to a driving shaft. In the same way the second, fourth and the sixth cages form an aggregate mounted on the other shaft. The machine is driven from the same shaft by means of two belts, one of which is straight and

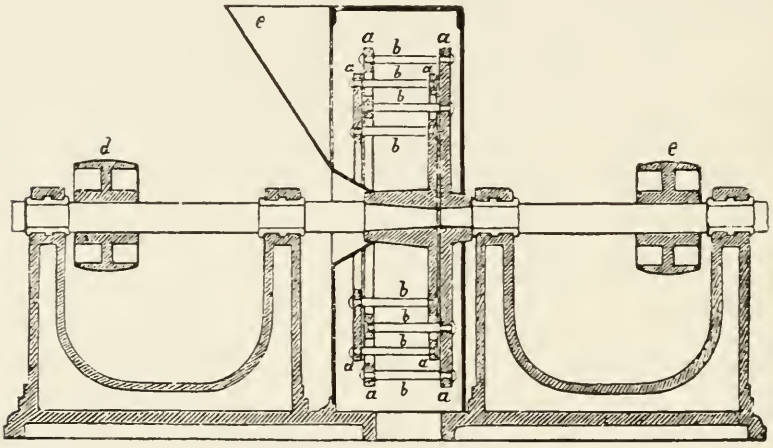


Fig. 29.—Carr's Disintegrator.

the other crossed, so that the cages formed by one of the elements of the drum fit into the annular spaces of the other and turn in a contrary direction. The machine is generally enclosed in a tight cover and surmounted by a hopper *e*, into which the material to be pulverized is charged. These fall into the interior cage, and the machine being in motion, they are projected by the centrifugal force across the bars of the first cage into the second; turning in an opposite direction from the second they are projected in the same way into the third which turns in the same direction as the first, then into the fourth, and so on. Finally, they are projected on the outside on all the points of the periphery through the bars. The operation does not last a second. This rapid grinding is not astonishing if the great number of shocks to which the matter is subjected be considered; the power of these shocks consists in the sum of the speed of the substance in one direction and of the bars of the cage in the other.

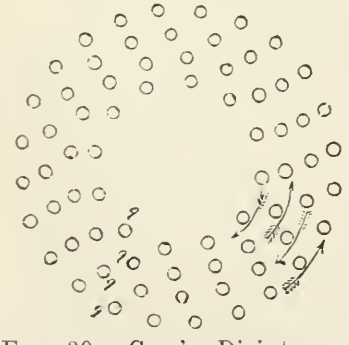


Fig. 30.—Carr's Disintegrator. Plan of the Cylindrical Cages.

The substance issuing from the crusher falls into a side channel hollowed out of the foundation of the machine, from there it

collects in the receiving vessel of an elevator, which removes it. The size of the drums, number of revolutions a minute, the force and the number of bars, vary according to the nature and the quantity of the material to be treated and according to the fineness to be imparted. A product, consisting of granules of no matter what size, can be obtained by turning the drums at a greater or less speed and using a suitable distance between the bars. The experience of the constructor is here the best guide. Carr's disintegrator is one of those which utilizes, to the best advantage, the energy which is transmitted to it, which explains its extraordin-

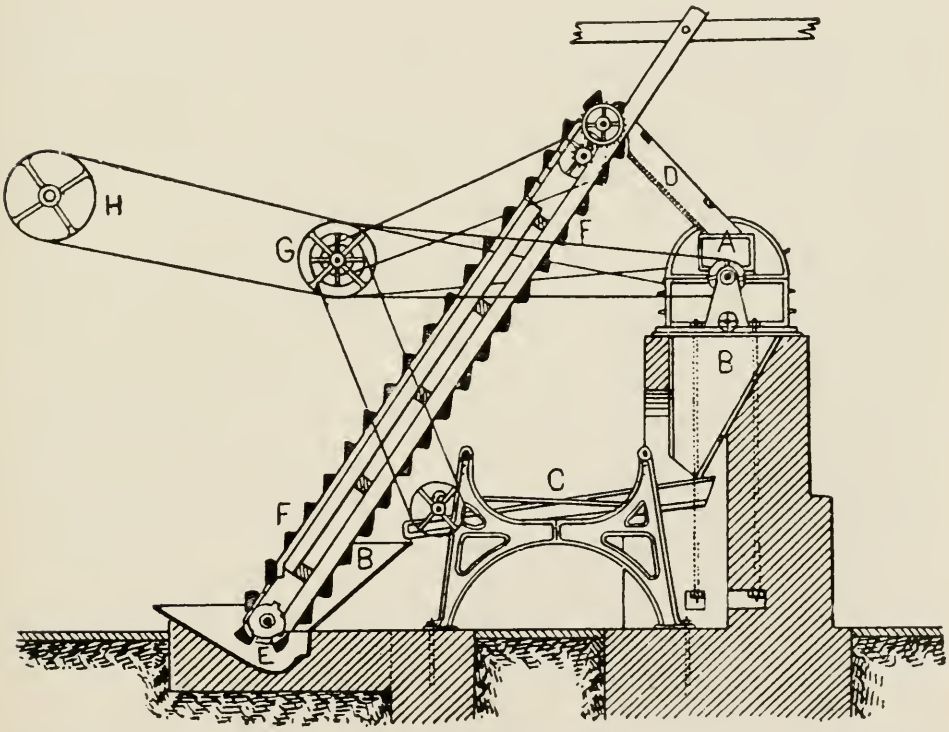


FIG. 31.—Carr's Disintegrator or Toothed Crusher. C. Sieve. F. Elevator. G. H. Transmission Shafting.

ary high output compared with other disintegrators, of whatever nature. It is used, not only for crushing superphosphates, but also for degelatinized bones. It also renders good service in making compound manures provided that the ingredients possess the same or but slightly different densities.

Cylindrical Crusher Fitted with Teeth.—This crusher consists essentially of a cast-steel foundation, on which are mounted two rolls, one of which is smooth, and the other lined with steel teeth. The first of these rolls has a diameter of 350 mm. (say about 14 in.), and makes 100 revolutions a minute. The second has a

diameter of 290 mm. (say 11½ in.), and makes 1000 turns a minute. This latter roll consists of a cast-steel nucleus on which are mounted toothed rings, easy to remove and replace. The machine is surrounded by a protecting cover, with a hopper, into which the material to be ground is fed. The substance passes between the rolls where it is subjected to powerful grinding, produced both by the steel points and the differential speed of the rolls. The machine frees itself automatically from all adherent matter, which is not so with Carr's disintegrator. It is particularly suitable for moist gluey superphosphates.

Cylindrical Crusher with two Rolls fitted with Teeth.—This machine is used for the same purpose as the foregoing; it is, moreover, used in making compound manures from superphosphate and sulphate of ammonia. The two rolls have a length of 500 mm. (say 20 in.) by 500 mm.; the one turns slowly, the other rapidly. The teeth of one of the rolls pass through the interstices between those of the other, and thus exert a powerful crushing action on the material. It is fitted with a cover forming a hopper, and is combined with an elevator and a shaking sieve. These machines may be grouped in two ways, according to the nature of the superphosphate. The crusher may be installed at a higher level than the sieve, or on the floor. In the first case, the superphosphate is fed into the receiver of an elevator which discharges it at a higher level into the hopper of the crusher. The superphosphate after passing through the jigger falls on a shaking sieve, the fine material passes through the sieve and falls into the discharge hopper, whilst the core in the sieve returns to the elevator, which brings it back into the crusher, and so on.

In the second case, where the crusher is fixed on the floor, the matter is charged directly into the crusher, from whence it falls into the cup of the elevator, which spreads it over the sieve higher up. The routine of the operations is absolutely the same as in the first case. But this second method has drawbacks. The cups of the elevator in seizing the material, crush it and transform it into a pasty gluey mass which resists sifting and returns, incessantly, from the sieve into the crusher again, to take the same road and choke up the whole of the apparatus. This drawback disappears if the machines be grouped in the manner indicated in the first instance, in which the superphosphate is elevated before being crushed; it is then in consistent lumps and stands the action of the cups very well. The sieve itself consists of a shaking table animated by a to and fro motion driven on each side by a pulley and crank. The frame of the sieve is hung in an iron frame, on which the driving pulley is mounted. The sieve is wire woven. It must be kept perfectly clean so that the superphosphate passes through and does not return to the crusher or become gluey. If the sieve

be obstructed, the machine must be stopped and the sieve cleaned. It is cleaned by beating and scraping with a broom, using sand if need be. A mechanical beater is often installed on the sieve, but it can only be used for cylindrical sieves. The latter again can only be used for very dry superphosphates, because in spite of the mechanical beating they are rapidly obstructed and difficult to clean.

If the superphosphate is in a pulverulent condition, it is simply sifted without crushing; only the core from the sieve then passes through the crusher at a lower level, from which it falls into the receiver of the elevator, which spreads it again on the sieve. The elevator, crusher, and sieve act simultaneously. However, it is better to drive the crusher independently, or by an electric motor, for in many cases the core on the sieves is not important, and the action of the crusher only intervenes usefully at rare intervals. It is hardly necessary to say that these machines should be easy of access. Fig. 31 represents a unit consisting of elevator, crusher, and sieve, mounted on iron frames. This unit, movable on rollers, may easily be conveyed from one depôt to another as required. Manipulations and cost of conveyance, often heavy, are thus avoided. An installation of this nature only requires three workmen. The first feeds the cups, the second looks after the machine and bags up, the third conveys the superphosphate to the depôt. In case of a break-down the three mutually assist each other. It is to be noted that damp weather is bad for grinding and sifting; the superphosphate is very deliquescent, and adheres to the machine.

Artificial Drying of Superphosphate.—If it be hardly possible to effect economy in crushing and dissolving with the machinery described above, it is quite otherwise with the operations relating to the finishing of the superphosphate, that is to say, those that intervene between "dissolving" and dispatch of the finished product. There are factories where these operations cost double what is required in a rational installation. In the present economical conditions of the industry, it is necessary to supplant ineffective hand labour, always costly, as much as possible by mechanical methods; a machine can be stopped when desired, whilst hand labour must be kept on continually, otherwise it goes. It must, therefore, be reduced to a minimum, the superphosphate finished with the least possible delay, without having to store it for a longer or shorter time, to render it saleable. In this chain of reasoning, the attention of manufacturers is drawn to the machinery and processes described further on.

Theoretical Review of Drying.—The moisture of a superphosphate is not wholly due to a high water content per cent, but also to the presence of an important proportion of free phosphoric acid in supersaturated superphosphates. Thus, when a superphosphate

contains 5 per cent of orthophosphoric acid it may contain up to 15 per cent of water, without being actually wet. According to Stocklassa, acid phosphate of lime heated to 100° C. loses, in ten hours, 1·83 per cent of water; in twenty hours, 2·46 per cent; in thirty hours, 5·21 per cent; in forty hours, 6·32 per cent; in fifty hours and upwards, 6·43 per cent constant. At 260° C. phosphoric acid changes slowly into pyrophosphoric acid.

$$2H_3PO_4 - H_2O = H_4P_2O_7.$$

Moist superphosphate may be dried by evaporating the water which it contains, either by absorbing a part of the free phosphoric acid which it contains by inert material, such as calcined gypsum, which combines chemically with the water, kieselguhr, peat dust, sawdust, or in fact by combining a portion of the free phosphoric acid. From an industrial point of view, we have to examine the application of heat to drying, direct heating, and cold drying. The drying machine, by direct heating, utilized for drying bones, may be used as in the drying of raw phosphates, sulphate of ammonia MP 140° C., beyond which it volatilizes, but it does not suit for superphosphate. It is, moreover, very trying and dangerous for the health of the workmen owing to the disengagement of the acid gases of the superphosphates. Besides, the material being pressed by the workmen during shovelling, readily sticks to the plates, and undergoes a sort of combustion from which a retrogradation of as much as 4 per cent may result. Moreover, it is very difficult to regulate the heat of a coal fire, which requires constant attention. The principal systems of drying in actual use are the following:—

Lambert's Dryer.—The inventor gives the following deliciously laconic description: The apparatus consists of a masonry chamber divided into three compartments: (1) A hearth of refractory materials, in which there are mixed the hot gases from the generator hearth and the air propelled by the blowers. (2) A chamber succeeding the preceding one, into which pass the mixture of gas and hot air before entering the drying machine. (3) A stove heated by the heat radiated from the hearth, and in which the apparatus described below moves. The dryer, properly so-called, has the form of a highly-elongated truncated cone and is arranged horizontally on rollers; it is entrained by means of gearing in a continuous system of rotation. In the interior this apparatus is fitted with corners intended to raise the material in an uninterrupted manner and to project it into the hot current during its whole stay in the apparatus. At the extremity of the small diameter of the apparatus is a feed hopper, at the other end are apertures, the object of which is to drop the dried material and allow the escape of hot air and steam during evaporation.

Zimmermann's Drying Machine. — Zimmermann's drying machine consists of an oven 8 metres (26 feet) high, heated by combustion gases. The hot air comes in contact with the material on iron plates suspended by chains and fitted with a system of agitation. An oven of this kind, occupying a space of 50 square metres (538 square feet), dries four wagons of superphosphate in twenty-four hours. The latter only remains exposed two minutes to the heat of a very bright coke fire; it there becomes heated to 80° C. and loses 5 to 6 per cent of water. The motor power to shake the plates is three horse, and the coke burnt, in twenty-four hours, half a ton. Three men can work two ovens. The iron plates have the drawback of not allowing the hot gases to pass, which thus take the shortest path along the sides of the oven. Lately the inventor has replaced them by sieves. The combustion gases and the acid gases pass into a dust chamber, where the latter is deposited, whilst the acid gases are purified in a condenser tower. The acid contained in the gas which is disengaged from the dryer is chiefly hydrofluoric acid. This gas, as well as the hydrofluosilicic acid, exists dissolved in the superphosphate water, and is partly re-formed when the substance is heated, the sulphuric acid, as CaH_2SO_4, [?] acting then on the still undecomposed calcium fluoride. The hydrofluosilicic acid is decomposed by heat into hydrofluoric acid and silicic fluoride.

The drying machine forming the object of the German patent 85,273, only differs from the above oven in the arrangement of the interior and in the method of agitation. The shaking plates are not suspended by chains, they rest on cross pieces and are moved by manuals.

Möller and Pfeiffer's Drying Machine.—Möller and Pfeiffer have constructed a drum drying machine in which they have striven to avoid shocks and sudden motion, which are absolutely injurious to the structure of superphosphate. On the other hand, these makers secure energetic ventilation by superheated air. This apparatus is based on this principle, that each matter requires appropriate treatment according to its nature. It consists of four principal parts, which are: (1) A heating system for heating dry air. (2) An exhauster for ventilating and absorbing combustion gas. (3) An arrangement for mixing air with the combustion gas, and to receive the superphosphates. (4) The drum, properly so-called. The working is as follows: The superphosphate is fed from a cup elevator into a hopper where it falls into the drying machine, where it is seized by a strong current of hot air, which dashes it into the rotating drum. The current of hot air is produced by a powerful fan with a conical aperture; the jet of compressed air that issues from this aperture drives an ejector which absorbs the combustion gases. The air and the gas are mixed in varying proportions at the will of the operator,

who can thus obtain whatever initial temperature he desires. This temperature may be somewhat high without there being any reason to fear retrogradation in the superphosphate treated, for the drying of the latter is so energetic that the temperature of the gas lowers considerably. Owing to the rotation of the drum and its sloping position the superphosphate circulates to the opposite extremity and is reduced to crumbs, consequently the interior of the granules is laid bare and submitted in its turn to the action of the hot gases. At the end of the drum the superphosphate falls into a "den," from which it is taken to be stored. The hot air which comes from the drum is not saturated with moisture; it is therefore in great part absorbed by the exhauster, mixed again with combustion gases, which bring it to the desired temperature, and afterwards it is again sent in to the drying machine, to carry on the work of desiccation. In this way the gases having already served, and still

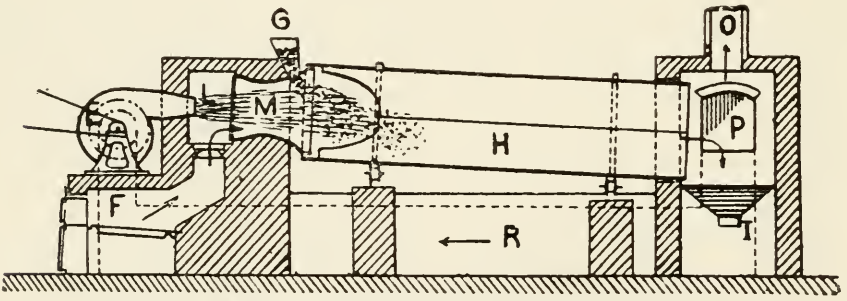


Fig. 32.—Möller and Pfeiffer's Dryer (vertical section).

at 85° C. (165° F.) are again utilized, only the small quantity required for rational working of the combustion is allowed to escape into the air, the loss of heat is reduced to the difference between the exterior temperature and that of the escaping gases. However, this circulation cannot be indefinite, it is limited, naturally, by the final saturation of the escaping gas. It is then necessary to start once more with completely renovated air so as to secure regularity in the drying. This drying machine is one of the best, and has received numerous applications.

Heymann and Nitsch's Process for Drying Superphosphates.—Heymann and Nitsch try to utilize the heat produced by the reaction of fresh superphosphate to vaporize the water brought to the surface of the lumps by crushing. They manage in this way to conduct drying and crushing simultaneously. The superphosphate, at a temperature of .90° C., is charged into slightly inclined rotary drums, the angle of inclination of which may be regulated at will. It is there crushed and sifted. The fine flour falls from the drum into a pit, and when it is cooled it has acquired the necessary degree

of dryness. But this condition, being incapable of being realized in the manner indicated, the inventors remedy it by injecting a current of hot air to meet the superphosphate as it falls from the machine into the pit. This process does not appear to have been adopted in practice.

Dr. Lorenz' Process (Dr. Lutjens' successor).—Dr. Lutjens has endeavoured to impart great rapidity to all the stages of superphosphate manufacture. With him it is a case of terminating the whole series of operations in twenty-four hours, so that the product may be warehoused or dispatched. The process which he uses is kept secret, and Dr. Lutjens has refused to give the author any

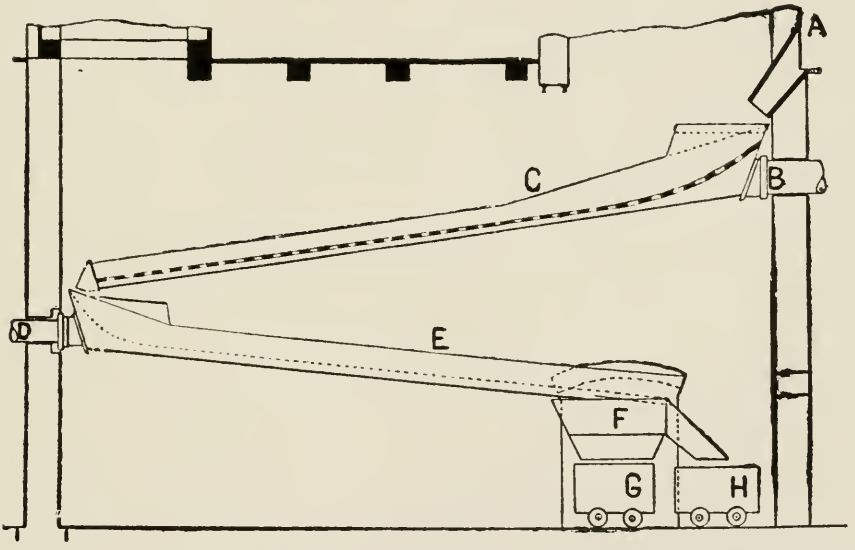


Fig. 33.—Lutjens' Superphosphate Dryer. A. Entrance of superphosphate from "den". B. Entrance for hot air under pressure. C. Drying trough. D. Entrance of cold air under pressure. E. Cooling trough. F. Sieve. G. Fine superphosphate. H. Core.

information. Although his process more particularly interests German manufacturers, who are obliged to make high strength superphosphates, sold according to their content of phosphoric acid soluble in water, the author thinks it his duty to give the description for the edification of his readers. The superphosphate, whilst at 100° C. (212° F.) in the "den," is taken by a conveyor on to a platform, under which a scraping machine works, and run into the top part of the latter, through a hopper. The scraping machine, and its application, are the object of German patents 95,756 and 96,046, the author's translation of which from the original German follow, the translations at the end of the *brevet* being almost unintelligible.

German Patent No. 95,756 *of* 16 *March*, 1897, *Delivered to the Chem. Fabrik Aktien Gesellschaft Vorm Carl Scharff et Co., Breslau.*

—The object of the new process is to divide superphosphates, so as to facilitate their distribution in the soil, for, in the state of lumps, they only give up their phosphoric acid slowly and difficultly. Besides, the fine division of a superphosphate is indispensable from the point of view of the actual manner of distributing manures by the manure drill, which greatly facilitates the work of the farmer. The superphosphate, such as it comes from the mixing "den," contains about 15 per cent of water, and in that condition it is very sensitive to shocks and crushing, so much so, that the processes used to pulverize it up to now are unsuitable. The new process is based on this observation, that hot solid superphosphate such as it exists in the mixing "den," possesses a property which has not been hitherto recognized, that of being capable of being cut into very fine slices, which exposed to the air break up and fall to powder. The process of which the present patent is the object, consists precisely in cutting the mass in very fine slices in the condition in which it comes from the mixing "den". Practically that is done as follows: the superphosphate is run into a drum in which knives, animated by a very rapid motion, cut (scrape) the superphosphate so as to divide it without crushing it. The thin slices are then reduced to a fine powder, the tenuity of which facilitates the expulsion of the moisture contained therein. The product thus obtained can be very easily and uniformly distributed.

German Patent No. 96,046 *of* 16 *March*, 1897. Addition to patent 95,756 of 16 March, 1897, delivered 19 March, 1897, maxima duration, 15 March, 1912.—The process of which this patent is the subject, is a form of application of a process claimed in chief patent, above-mentioned, the object of which is to cut up fresh superphosphate in a rotary drum armed with knives. Up to now the superphosphate from the "den" was stored, and as soon as it was cold and dry, it was pulverized in a crusher. As it comes from the "den" the superphosphate is hot and soft, on cooling it becomes consistent. It has been remarked that only the superphosphate which comes from the den in lumps becomes consistent, whilst the portions that are in a pulverulent state do not agglutinate but remain in the condition of powder in spite of the pressure of the mass and the high temperature. This observation has suggested the idea, that superphosphate could be reduced to a dry and pulverulent condition as soon as it comes from the mixing "den". The crushing process used hitherto, such as passage through a Carr's disintegrator, cannot be applied to fresh superphosphate because they would render it gluey. The present invention enables the desired state of division to be imparted to superphosphate immediately it comes from the mixing "den" without grinding or crushing it. The process employed for the purpose is based on this fact, that if superphosphate is cut into very fine slices in its actual condition it is immediately

converted into a fine powder. The superphosphate is transferred by a conveyor into a hopper which feeds it into a drum armed with knives. This drum consists of a posterior disc and an anterior ring. Between the disc and the ring there are arranged tangentially at fixed distances steel blades or knives, covering the openings for the exit of the finished superphosphate. Sixteen blades of this sort pass in front of the hopper aperture, at a speed of 300 revolutions a minute, consequently 4800 blows per minute. The slices so produced are very fine and do not set on accumulating. The drum is driven by shaft and pulley. On the hopper side and beneath it are wrought-iron plates, on which the finished superphosphate, issuing from the drum, falls; from these plates it falls into trucks. The working of the installation is as follows: The drum is driven by a pulley and turns at great speed. This speed, which is thus transmitted to the knives, is calculated in such a way as to exceed the rapidity of the fall of the superphosphate into the feed hopper. In that way, all the superphosphate is forced to pass over the knives, and the uncut lumps are prevented from passing through the apertures and falling into the truck. The spaces between the knives are regulated according to the speed of the periphery of the drum and reciprocally. It follows that the knives succeed each other in their action, penetrate into the material and scrape it through successive layers. Very thin slices are thus obtained, which fall to powder. This division is still further favoured by the speed of rotation of the drum, which produces a strong current of air acting on the substance, and producing a cyclonic motion in the parts detached by the knives. The pulverized material falls from the plates into a truck. The current of air produced by the rotation of the drum imparts a certain speed to the phosphate powder detached by scraping. The wrought-iron plates also serve to turn this current of air in its tangential course, so that the powder only falls into the trucks at the speed it would fall by its own weight. The too abrupt fall of the material is thus avoided. Finally, the current of air produced in the drum frees the superphosphate from any gases with bad odour, and expels them outside.

Dr. Lutjens afterwards modified his processes, first, in combining drying with the scraping machine, afterwards in cooling the dried superphosphate. The process thus modified realizes to the letter the problem enunciated above, to produce a superphosphate ready for dispatch in twenty-four hours. For this purpose the superphosphate cut in very fine slices, falls into an upper drying trough, where it is exposed on all sides to the action of hot air; this completely traverses the mass, heats it and renders it friable. From the upper trough the superphosphate falls into a second trough placed underneath, where drying is completed by a current

of cold air under pressure, which lowers the temperature to 20° C. The superphosphate is then sifted; it quits the sieve in a very fine state, ready to be dispatched. The cold air treatment not only prevents the substance from aggregating into lumps, but it at the same time prevents retrogradation, as will be seen later on. The plant dries [it is claimed] 10 tons of superphosphate per hour. It requires few repairs. Fuel is well utilized, for on burning ordinary coke, only 1 cwt. per 5 tons of superphosphate is used to remove 5 per cent of moisture.

It is right to add that to work regularly, this machine requires to be manned by workmen familiar with this class of work; it increases the output of the factory, and superphosphate can be dispatched from the heap.[1] The cooling of the superphosphate was the object of the German patent No. 112,151 of 14 April, 1899, of which the following is the translation. The processes employed up to now for drying superphosphates have the drawback of leaving these products at a high temperature, so that if run on to a heap they only cool very slowly. Now, heat is very injurious to the superphosphate in the heap, and it then acquires a great tendency to form lumps. Under the pressure to which it is subjected by its own weight, it becomes compressed more strongly the longer the warehousing is prolonged, and it is then necessary to pulverize it once more before dispatching it. To this drawback a graver one has to be added, stored superphosphate has a great tendency to retrograde, the phosphoric acid rendered soluble then returning to the insoluble condition, because heat favours retrogradation and the dried superphosphates preserve their heat when in high heaps, and only cool slowly. The object of the present invention is to avoid retrogradation of the soluble phosphoric acid in superphosphates which have to be stored. For this purpose the heat is removed from the dried, hot, pulverized superphosphate by a current of cold air. The conveyance of the superphosphate thus finished, to the store, is done in tilting trucks or by ærial conveyor. This latter system is the best and the most economical in the manufacture of superphosphates, where it is indispensable to utilize as much as possible the covered space to store the goods. This is what a manufacturer who uses the Lutjens process says: "I could not be better satisfied with the scraping machine. The superphosphate obtained by this process is exceedingly fine, free from lumps, and so dry that it may be dispatched a few days after it is cooled. It responds to all exigencies. Before dispatching it I pass it through a sieve of 6 mm. (a quarter inch sieve), and I get no

[1] With say three screens on to a heap, one man with a pick is occupied in "getting" the superphosphate for the other six men—two men to each screen —a left-handed man mated with a right-handed man, but most men accustomed to this class of work are ambidextrous.—Tr.

core. The scraping machine enables superphosphates, of a quality hitherto unknown, to be made cheaply." Dr. Riemann, a master of superphosphate manufacture, says: "We have only 0·5 to 0·7 per cent of insoluble P_2O_5 in Florida superphosphate. As a general rule we obtain an increase in the phosphate rendered soluble, and we have not observed retrogradation in Florida superphosphate even after several months' storage."

Superheated Superphosphates.—Crispo draws attention to the changes which occur in overheated superphosphates. After a certain temperature orthophosphoric acid is changed into metaphosphoric acid. Experiments on this point have shown that orthophosphoric acid, heated to 105° C. during three hours, is converted into metaphosphoric acid to the extent of 10 per cent, whilst if heated to 200° C. it is converted to the extent of 90 per cent, by the loss of a certain amount of combined water. If the soluble phosphoric acid by the citrate method be determined in overheated superphosphates, it is to be observed that metaphosphoric is not precipitated by magnesia mixture, and that only the orthophosphoric acid is found in the precipitate. If the determination be made by the molybdate of ammonia method, the sum total of the two phosphates is found, the nitric acid bringing the meta back into the ortho form. Crispo considers metaphosphoric acid of less value than the ortho. However, experiments made in Germany have shown that under the first of these two forms phosphoric acid has given good results. Experiments at the Agronomical Station of Gomblouse, by Grégoire and Hendrich, have shown :—

1. That the alterations undergone by the dried superphosphate in no way diminish the fertilizing value of that product.

2. That desiccation at a temperature of 165° C. has appreciably increased the activity of the phosphoric acid.

3. That the metaphosphate and the pyrophosphate of lime respectively, the products of dehydrating mono and bicalcic phosphates, are without fertilizing value. In pot culture experiments in the Liége laboratory, each of the pots containing 4 kilos (8·8 lb.) of soil, Ligouro oats gave, on an average, according to the phosphates used :—

TABLE XLII.—RESULTS OF EXPERIMENTS WITH ORDINARY SUPERPHOSPHATE AND SUPERPHOSPHATE DRIED AT DIFFERENT TEMPERATURES ON LIGOURO OATS.

Phosphate used.	*Grain and straw gr.*	*Proportional yield.*
Without phosphoric acid . . .	12·3	100
Ordinary superphosphate . . .	28·8	234
Superphosphate dried, slightly calcined .	26·9	219
Metaphosphate	19·3	157
Superphosphate dried at 160° C. . .	28·8	234
,, ,, ,, ...	27·6	224

These results show that superphosphate dried at 160° C. and slightly calcined, produce the same effects as ordinary superphosphates. On the other hand, the action of commercial metaphosphate is comparatively feeble in the sandy clay experiments. In an experiment on sandy soil the dried and calcined superphosphate had a less effect than superphosphate simply dried at 160° C. (320° F.).

Drying Superphosphates in the Cold.—Cold drying processes consist essentially in mixing dry substances intended to combine with a portion of its phosphoric acid with the superphosphate. Rumpler advises the use of bone black and degelatinized bones. These substances possess a great absorbent power and may be used with success for the drying of high strength superphosphates. As regards the use of bone dust, 1 per cent may be added to the superphosphate, according to its percentage of free acid. The bone dust should pass through a 70 mesh sieve. The phosphate taken from the "den" is spread out, the bone dust sprinkled over it, the mass turned over and passed through an inclined screen. After twenty-four hours the bone dust is almost all dissolved, and the superphosphate may be dispatched. It is clear, however, that this work done by hand can only partially attain the object in view. Dr. Klippert has the merit of applying this principle by means of an improved equipment, the construction of which is kept secret.

Drying of the Superphosphate by Dusting and Mixing in the Georges Crusher-Sifter.—In France an analogous process to that just described is adopted. This process consists in mixing 3 per cent of raw Gafsa superphosphate well dried and in the condition of fine powder. For this purpose the superphosphate from the "den" is spread by an aerial conveyor on a platform (Fig. 34); a workman dusts the product with Gafsa superphosphate and charges it into the grinding sifter shown in the figure. In this machine a shaft with blades driven at a suitable speed triturates the mass and mixes it intimately, whilst the sieve turns it in a contrary direction. The fine material falls from the sieve into the bin of an aerial conveyor which conveys it to the warehouse, where it remains until the time for delivery. Before being dispatched the superphosphate is crushed and sifted through the Coster crusher. When the superphosphate is suitably prepared, the treatment indicated suffices to obtain it dry. A great number of factories have installed this process, which enables them to dispense with a drying machine. It is necessary to add that it is only applicable to superphosphates for home consumption, as superphosphates intended for exportation, especially those for the East, ought to be dried artificially in the drying machine. In the Lutjens process, 1 per cent of degelatinized bones is also added, or Algerian phosphate, so as to dry the product and avoid the formation of lumps. The choice between

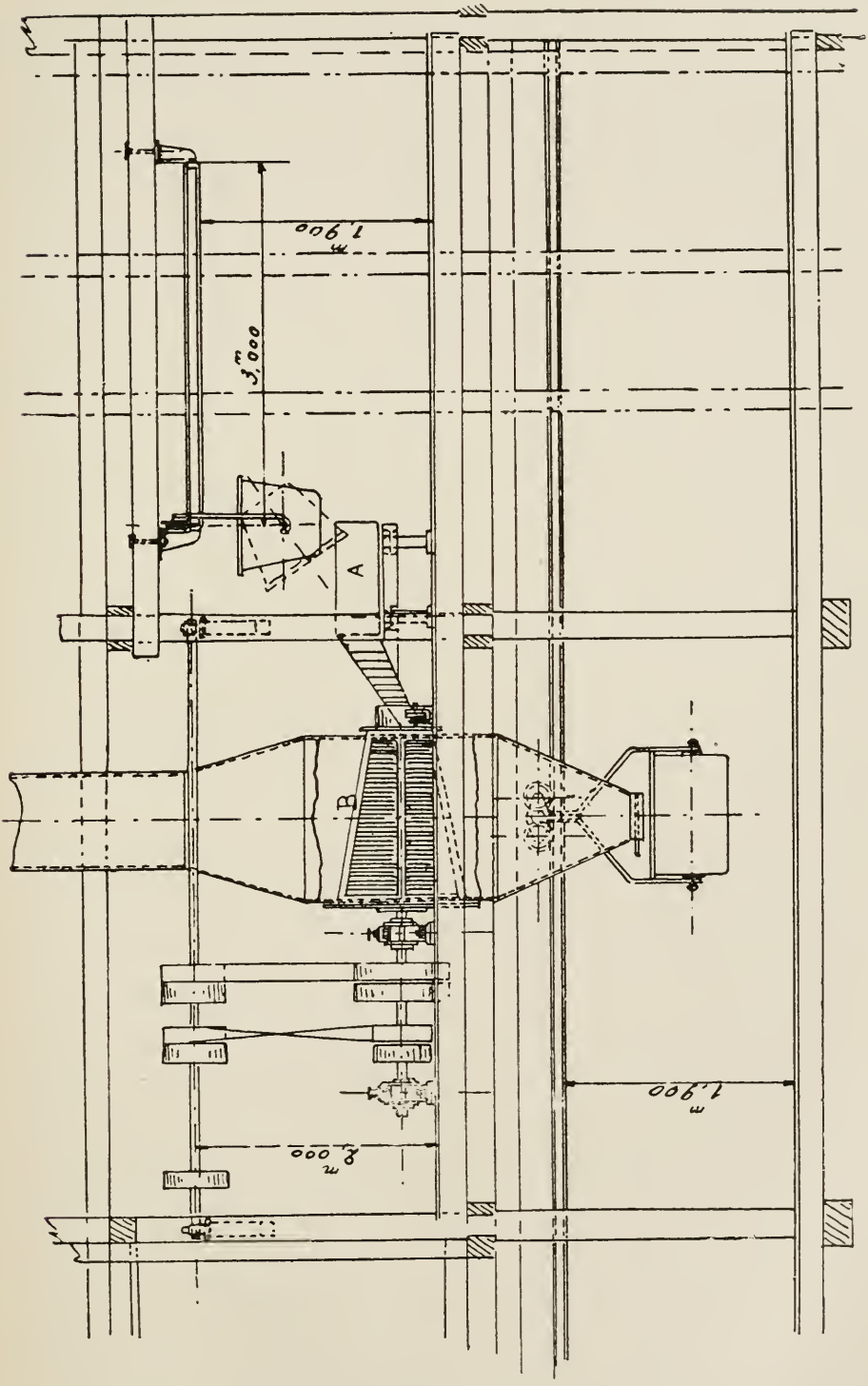


FIG. 34.—Sifting Crusher (Benker and Hartmann).
A. Table for dusting superphosphate. B. Sifting crusher (double motion), Georges system.

bone dust and Algerian phosphate, as the drier to be added to the superphosphate, depends on circumstances. If the superphosphate is to be dispatched in a week or thereabouts, one remains satisfied with 1 per cent of Algerian phosphate. On the other hand, if it should not require to be dispatched before a month or six weeks, 0·5 of bone dust and 0·5 per cent of Algerian phosphate is added. When the phosphate has to be kept longer, 1 per cent of bone dust is simply added. The reason of this method of proceeding is, that the addition of the phosphate tends to harden the superphosphate in the heap so that it has to be screened again before dispatch, or even passed through Carr's disintegrator. The new methods of Lutjens for the working of superphosphates present real advantages. But such installations are somewhat costly; moreover, they are only used where high strength superphosphates are required or when agriculture requires pulverulent products capable of being spread by the drill. It is necessary, in that case, that the superphosphate contain an important proportion of free phosphoric acid intended to dissolve the raw phosphate added as mentioned above. A Florida superphosphate of 18 per cent, for example, should not contain more than 4 to 5 per cent of free phosphoric acid if it be not desired to add raw phosphate thereto; if on the other hand 1 per cent of Algerian phosphate be added thereto, the free acid may be increased to 7 to 8 per cent. Certain foreign countries stipulate for superphosphates of very high strength. Thus Scandinavia stipulates for 20 per cent, which is nonsense, as products of this kind run relatively dearer than 15 to 18, which are current types.

Storing (Preservation) of Superphosphate—Retrogradation (Reduction) of Phosphoric Acid.—Superphosphate keeps well from one season to another when the phosphate from which it was made does not contain more than 2 per cent of sesquioxides, but it is not so if kept longer. The phosphoric acid of the superphosphate commences to retrograde ("reduce") if the raw phosphate was not pure. Retrogradation sets in much sooner if the raw phosphate contained more than 2 per cent of sesquioxides, or if mistakes have been made in its manufacture. Retrogradation ("reduction") occurs under the influence of different causes, physical and chemical. The heat and pressure of the superphosphate heap appear to be the direct predeterminating causes. Stored superphosphate forms, first of all, packed layers. The granules of which it consists have only a slight superficial contact, but as the thickness of the layer increases the substance compresses in virtue of its own weight, afterwards in virtue of the length of contact, so that finally the particles are glued together to form a very compact mass. There is thus established between each an exchange of chemical energy which means decomposition. Experience shows that these changes are more

rapid in moist hot superphosphate than in dried cooled superphosphate. The crystallization of the sulphate of lime, unfinished in superphosphate, stored hastily, is completed in the superphosphate heap. The superphosphate of lime, combining with the sulpho sesquioxides, forms once more sulphate of lime ; free syrupy phosphoric acid acts on the silicates, etc. Now, all these reactions give place to a disengagement of heat, consequently the matter expands and tension is produced. Each of these reactions occur at a fixed temperature, which it is impossible to gauge directly owing to the isolating influence of the sulphate of lime. Finally, agglutination is still further induced by the rarefaction of the air between the granules cooled in the heap. For a difference of 10° C. (18° F.) the difference is 3·5 per cent. It has been observed that the phosphoric acid of the superphosphate does not commence to retrograde ("reduce") until the moment when the particles agglutinate, i.e. when it is subjected to a fixed pressure. It is, therefore, pressure which causes retrogradation by destroying the friable compounds of the superphosphate. The part played by temperature has also been determined by direct experiments. These show that it may rise to 100° C. without hurting pulverulent friable superphosphate, and up to 50° C. for agglutinated superphosphates higher temperatures are only injurious under pressure. Smetham, in examining the influence of the oxides of iron and alumina on the retrogradation of phosphates, observed an essential difference in the action of the two oxides, as had been observed for a long time in actual practice. Whilst 1 part of oxide of iron will cause 2 parts of phosphate of lime to retrograde, the oxide of alumina can only retrograde its own weight of phosphate (theoretically it retrogrades 3 times its own weight). In Florida phosphate, Pebbles and River phosphate, the greater part of the sesquioxides are present as alumina. The ratio of the alumina to the iron is, on an average, 1 to 0·4. According to the same authority, iron forms two insoluble compounds, the mono-di-ferri phosphate and the di-tri-ferri phosphate ; alumina only forms one compound. The free ortho phosphoric acid would appear to be rendered insoluble in the soil more rapidly by iron and alumina compounds than monocalcic phosphate, as previously determined by Gerlach ; the latter also remarks that phosphoric acid, combined with oxide of iron and alumina, does not dissolve in carbonic acid water, contrary to what occurs with the acid combined with lime or magnesia. Phosphates of iron and alumina are only very slightly soluble in the solutions of organic acids ; phosphate of iron is almost insoluble therein. As the moisture in the soil is not more acid than this artificial solution, it may certainly be taken for granted that the phosphates of sesquioxides remain insoluble in the soil. When retrogradation starts nothing can stop it ; it pursues a very rapid course, even when the cohesion of the matter is

broken, as is the case when orders are being dispatched. When superphosphates of this kind arrive at their destination they sometimes yield, on analysis, different results from those obtained on dispatch, but the sample then retained shows identical results, which shows that the superphosphate retrogrades in sample bottles. If retrogradation cannot be stopped, nor the chemical action which determines it, one can in a way prevent it in a bad superphosphate. It suffices to dry it as completely as possible, store it cold, shorten the storage, or preserve the superphosphate in a thin layer in the beginning by spreading it over all the available space, extracting the lumps by sifting, using it to prepare superphosphate of ammonia (the sulphate of ammonia may hinder retrogradation) or low strength superphosphates. By mixing 10 per cent of wood sawdust of bad quality with an 18 per cent P_2O_5 superphosphate which had retrograded 1·5 per cent, it was observed that the phosphoric acid did not retrograde further in the low strength manure thus prepared. In this case the amount of liquid contained in the superphosphate $H_3PO_4 + H_2O$ lost 45 per cent of its mobility in consequence of this dilution. On the other hand, the superphosphate was loosened from its pressure, the latter being spread over all the ballast. It is clear that this remedy has limits, but it gives good results.

Forestalling Retrogradation by Schucht's Method.—To ascertain if a superphosphate is going to retrograde, and at what moment it will retrograde, are points which it is important for the manure manufacturer to know. Schucht has used for years a method which gives results appreciably agreeing with facts. It is generally very difficult to get access to the lower layers of a superphosphate heap. It is, therefore, impossible to analyse them, and another means of control must be found. This means is supplied by the retrogradation indicator about to be described. The apparatus consists of a graduated lever *a*, on which is a movable runner of 15 kg. (33 lb.). This lever is movable, round a point of support *b*, fixed on a fork *c*. A very strong flat-bottomed porcelain vessel *e*, is used to receive the superphosphate, which is compressed by means of the plug *f* fixed on the lever. The operation is conducted as follows: 100 grms. of superphosphate are run into the porcelain dish with 25 grms. of hot water, and the mixture crushed with the pestle; the excess of water is expelled on the water bath and the vessel is put under the press plug, which compresses the contents of the dish. The apparatus is kept under pressure for twenty-four hours at a temperature of 50° to 70° C. (122° to 158° F.), water, soluble phosphoric acid, and free phosphoric acid are estimated in the superphosphate, treated as above, after having already made the same estimations in the original superphosphate. By comparing the results of the two analyses a valuation of the superphosphate can be made. The differences existing between manufacturing localities and in storing

in no way influence the accuracy of the method. If the exact temperature and pressure be found, they remain the same in all cases so long as the raw material is not changed. This method is far from solving the question of retrogradation, but it is interesting, because an idea can be gained from it of the retrogradation of a given phosphate. Dr. Grueber gives the results of experiments which he has made with Schucht's apparatus, of which the following is a brief summary :—

1. A Florida phosphate, 35 per cent P_2O_5, and 2·52 of sesquioxides, when rendered soluble gave 18·7 per cent P_2O_5 soluble in water, and 1·21 of insoluble P_2O_5. Treated after Schucht's method, under a pressure of four atmospheres and at a temperature of 40° C. (104° F.) (the apparatus being home-made could not do better), it contained 18·2 per cent of P_2O_5 soluble in water, and 1·76 of insoluble P_2O_5. A second Florida phosphate, with 35·96 per cent P_2O_5 and 2·38 per cent sesquioxides, gave immediately

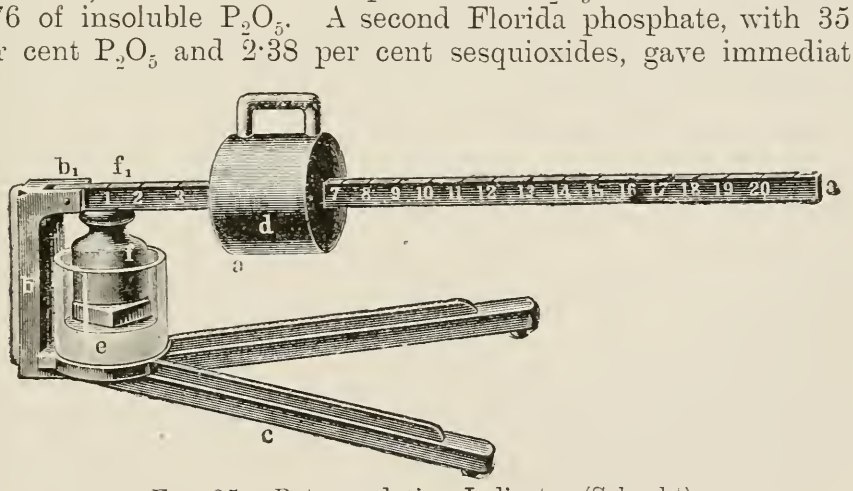


Fig. 35.—Retrogradation Indicator (Schucht).

after being rendered soluble, 18·8 per cent P_2O_5, and 0·81 insoluble. After Schucht's process, 16·67 per cent soluble P_2O_5, and 2·62 per cent insoluble, which shows the efficiency of Schucht's apparatus, that is to say, that the particles of phosphate, intimately mixed and pressed hot, show an accentuated tendency to retrograde.

2. A comparison was made with a superphosphate stored hot in a big heap. A Florida phosphate with 35·8 per cent P_2O_5, and 2·09 per cent of sesquioxide, was in use. This phosphate, tested immediately after being "dissolved," gave 18·40 per cent P_2O_5 and 1·1 per cent insoluble. With Schucht's method it gave 17·25 per cent soluble P_2O_5, and 2·06 per cent insoluble. The stored heap showed at the end of a year 17·28 per cent P_2O_5, and 1·96 per cent insoluble. Consequently the stored phosphate confirms the accuracy of Schucht's method. In the middle (height) of the heap a retrogradation of only 0·21 per cent occurred and no retrogradation in the top.

3. Another experiment was made with a Florida phosphate, with 35·49 per cent P_2O_5 and 2·25 per cent of sesquioxides. When "dissolved" it gave 18·98 per cent of soluble P_2O_5, and 0·95 per cent of insoluble. Schucht's method was applied in three ways, using a Schucht's instrument constructed by Kohler and Martini of Berlin, by which a higher temperature and pressure could be applied. The following are the results :—

(*a*) Pressure and average temperatures as above : 4 mm. (? atmospheres) of pressure at 40° C., 17·09 per cent soluble P_2O_5, 1·85 insoluble ; (*b*) increased pressure and average temperature : 7 mm. (? atmospheres) of pressure at 40° C., 16·67 per cent soluble phosphates, and 1·91 per cent insoluble ; (*c*) increased temperature and pressure : 7 mm. (? atmospheres) pressure at 70° C., 16·72 per cent soluble P_2O_5, and 2·28 per cent insoluble. It will be seen that retrogradation increases with the temperature and pressure. This superphosphate, though piled in a heap 16 ft. high, did not retrograde even in its lower part, which Dr. Grueber attributes specially to the storing of the superphosphate, after complete cooling, by Dr. Lutjens' scraping and cooling appliance. The fact that the cooled superphosphate did not retrograde is not surprising, because as far back as 1870 this important fact was observed in the case of superphosphates made from Lahn phosphorite, very liable to retrograde, that the more rapidly it was cooled the less the soluble phosphoric acid retrograded. Dr. Grueber concludes that, in order to explain retrogradation, decisive results will only be obtained by working on the large scale with superphosphates to which different materials have been added. With the data so obtained, the treatment of phosphates could be modified according to their composition and the manner in which they behave.

Dr. W. Paysan considers retrogradation is a rather exceptional phenomenon.[1] He supports his view by personal experiences with Algerian phosphates with 0·5 of sesquioxides, and Peace River Pebbles with 2·5 per cent of sesquioxides. The solubilization of the first was always pushed in a constant manner to 0·75 per cent of insoluble, that of the second to 1 per cent. He never found retrogradation in either even after long storing. He considers that in valuing phosphates up to now too much importance is attached to the percentage of sesquioxides. To prove it he quotes trial mixings he made with this end in view. It was a case of three Tennessee phosphates (*a*), (*b*) and (*c*) which are characterized from this point of view by containing 79 per cent phosphate of lime, 2·36 per cent oxide of iron, and 2·24 per cent of alumina, say a total of 4·6 per cent of sesquioxides. The results are given in the following table :—

[1] See note 1, p. 142.

TABLE XLIII. — SHOWING CHANGES IN COMPOSITION WHICH TENNESSEE SUPERPHOSPHATES UNDERGO IN FOUR AND A HALF MONTHS FROM DATE OF MAKING.

Mixings made 2 September, 1898.		Sample of same Superphosphate Analysed 17 November, 1898.	Sample of the same Phosphate Analysed 17 January, 1899.
P_2O_5 insoluble	*a* 2·27	2·35	2·30
	b 2·20	2·33	2·23
	c 1·98	2·32	2·48
Soluble $Al_2O_3 + Fe_2O_3$	*a* 0·90 + 0·26	0·65 + 0·17	1·14 + 0·17
	b 1·07 + 0·27	0·87 + 0·18	1·08 + 0·22
	c 1·28 + 0·29	1·09 + 0·22	1·22 + 0·16
Insoluble $Al_2O_3 + Fe_2O_3$	*a* — —	— + 1·21	— + 1·0
	b — + 1·05	— + 1·20	— + 1·12
	c — + 1·01	— + 1·17	— + 1·12
Free Acid	*a* 5·50	4·20	4·90
	b 5·50	4·30	4·80
	c 6·10	4·80	5·30

Paysan adds that not being able to find the cause of retrogradation in the sesquioxides, he tried to find it elsewhere, and he quotes the following case of a delivery of Florida phosphate. The samples taken the first day at four different points looked well ; the next day fresh samples were taken, this time going further forward than the points explored the day before, and it was found that in certain places the phosphate was darker than in others, and contained much impurity. Two samples of this kind, taken at two different points, gave the following figures :—

	a	*b*
	Per cent.	*Per cent.*
Phosphate of lime	71·97	64·65
Sand	8·85	19·00

An average sample of the whole cargo gave the following analysis. Phosphate of lime 77·73, oxide of iron and alumina 2·13 per cent. The pure phosphate behaved in a normal fashion. In working it dissolves completely and gives no retrogradation, but when wrought up with the impure part retrogradation was rapid, 1·52 to 2·14 per cent of insoluble was obtained against 0·75 with the pure superphosphate. This example well explains contradictions and obscure points. But Dr. Paysan does not admit the theory of pressure in the question of retrogradation. He has often remarked a tendency to retrograde in superphosphates as soon as they have gone through Carr's disintegrator. He does not ascribe transcendent merit to Dr. Lutjens' processes. He regards them as elegant and useful auxiliaries in superphosphate manufacture, but

which do not dispense with passing the manure through Carr's disintegrator.

Basis on which Superphosphates are Sold.[1]—In the beginning of the superphosphate industry, superphosphates were sold according to their percentage of phosphate of lime soluble in water. But there were disputes between buyers and sellers, the former not finding the strength given them by the latter. A portion of the phosphate had become insoluble on delivery. The British were the first to determine that that part of the phosphate originally soluble in water, and at the end of a certain time was no longer so, was, however, soluble in weak reagents, such as carbonate of soda or oxalate of ammonia, whilst the phosphate, originally insoluble, did not dissolve appreciably in these reagents. At first it was thought that this phosphate which British chemists called "reduced" phosphate, but now termed retrograde phosphate, was formed by the action of the monocalcic phosphate on the tricalcic phosphate producing an intermediate bicalcic phosphate. Such, at least, was the current explanation fifteen years ago. Be that as it may, manufacturers have got over the difficulty, not by improving their manufacture, but in altering the basis of sale of superphosphates, i.e. by selling them according to their content per cent of phosphoric acid soluble in cold alkaline ammonium citrate which they term assimilable phosphoric acid. This method of sale is evidently very convenient for the manufacturer, and enables the works chemist to cease from worrying over retrogradation whether it arise from bad manufacture or the presence of impurities in the raw phosphates.

Now, as Mr. J. Joffre observes: "When a superphosphate is treated with citrate of ammonia in analysing it, both the citrate

[1] A 25 per cent soluble phosphate, say phosphoric acid = 11·45 per cent, is the current British make of soluble phosphate. A 12 per cent Somme will give a 30 per cent soluble phosphate which will bear an addition of 3 cwt. of gypsum to the ton to bring it down to 25 per cent if the superphosphate is dispatched as soon as made. Or the gypsum may be partially replaced by a little Belgian phosphate. But in Britain it is not considered good business policy to add a nitrogenous manure like bone dust to a superphosphate, and the tendency of the workmen is always to use far more bone dust than that in the formula, for reasons which will be readily appreciated; the result being that when it comes to stocktaking the leakage of bone meal and bone dust is excessively large. What the translator cannot understand is the magical effect of 1·0 per cent of bone dust, say one-fifth of a cwt., i.e. 22 lb. to the ton. If the superphosphate was very damp such a pinch of bone meal would be a drop in the ocean; 3 per cent of raw Gafsa phosphate can be understood. It will readily be seen that only by strict book-keeping by double entry can the amount of phosphate and bone dust used as driers be controlled. The translator fears the author is somewhat over-sanguine as to the efficacy of some of the drying machines and grinding machines which he describes. It appears to the former that if a manure will dry naturally, as it should do, these machines are not so indispensable as would be inferred, and where the manure will not dry naturally one may be pardoned from doubting if the machines are quite so efficacious as one is led to believe.—Tr.

soluble phosphoric acid, and the water soluble phosphoric acid, enter into solution simultaneously. It results that when the analysis is made by the citrate method (without a separate estimation of the phosphoric acid soluble in water) there are confused together both the phosphoric acid soluble in water, of great fertilizing value, and the phosphoric acid combined with iron, which has but very little. The citrate method is, therefore, uncertain. The results may represent bodies which are very good for plants if they consist of monocalcic phosphate or free phosphoric acid which are dissolved in this reagent. They may, on the other hand, represent substances which only have a very mediocre action, if they are phosphates of iron, called retrograde phosphates, which have passed into solution. Analysts ought, therefore, to give preference to estimating by the solubility in water as in Great Britain, Germany, and the United States. They ought, at least, to estimate separately the soluble in water and likewise separately the citrate soluble."

It is now admitted, without going further, that there is no great difference from a fertilizing point of view between the water soluble phosphoric acid and the citrate soluble. There is, however, a sharp line of demarcation between the two products; the first is immediately assimilable by plants, the second is rendered soluble and assimilated in the soil to the same extent as the phosphoric acid in basic slag. But then there is no occasion for the difference in price between the selling price of superphosphates (supposing them to be partially retrograded since they are sold as such) and basic slag. Now this difference is considerable. On 1 January, 1909, for basic slag at Paris stations the price of the unit of phosphoric acid in basic slag and superphosphates was exactly in the ratio of 3 to 4, which makes the phosphoric acid in retrograde phosphates 25 per cent dearer than the citrate soluble phosphoric acid of basic slag. It is asserted, it is true, that if retrogradation has not already occurred in the superphosphate before spreading it occurs rapidly in the soil. The validity of this assertion will be examined later on in giving Dr. P. Wagner's opinion on the matter. In Germany superphosphates are sold by their content per cent of water soluble phosphoric acid, the citrate soluble not being taken into consideration. Now, in superphosphates containing 1 per cent of insoluble phosphoric acid this latter is two-thirds soluble in water; the manufacturer is thus prejudiced. In Spain and in the Mediterannean regions the customs are the same as in France. In Austria-Hungary customs vary with the localities; in some superphosphates are sold according to their content of water soluble phosphoric acid, in others according to their content of citrate soluble. It is the same in Russia. In America sales are also based on the citrate soluble which enables manufacturers to work low grade phosphates with a high percentage of sesquioxides. At

present it is Germany which manufactures the most chemical manures to respond to the increasing demands of agriculture.

Phosphatic Manures—Do they become Insoluble in the Soil ?—The benefits of enriching the soil in phosphoric acid has sometimes been questioned on the ground that phosphatic manures become insoluble in the soil, and consequently inactive in a period of time varying from one to three years. This objection has been refuted by Dr. Wagner. If superphosphate or basic slag be buried and the soil be left to itself without tilling it or sowing it, what happens? The result will be that the rain, filtering through the layer of soil, will insensibly dissolve the phosphoric acid of the superphosphate and the basic slag, and will transport it always a little further into the subsoil, where it comes in contact with oxides of iron, alumina, and lime. It will combine with these salts forming less and less soluble compounds, to pass finally after fifty or a hundred years perhaps, one does not know exactly, to almost the same state of insolubility as the phosphoric acid contained in the minerals in the soil.

"This transformation will require a very considerable time. It is also certain that in a cultivated soil tilled, laboured, sown, and manured, the process of being rendered insoluble is unceasingly opposed to the tendency to become insoluble; the cultivated soil opposes the contrary one, that of becoming soluble. The humic acid, the carbonic acid, the nitrate of soda, the roots of plants, fungi, bacteria, the circulation of air and moisture, are constant agents of activity which do not allow the soluble phosphoric acid to come to rest. As soon as precipitated phosphates are formed in the soil with a portion of the phosphoric acid whether from superphosphates or basic slag, the agents in the soil just enumerated exert their solvent action and bring back the phosphoric acid to the soluble state. the lime, alumina, and oxide of iron reprecipitate it again in part, the agents in the soil bring it back unceasingly to the soluble state, and so on. The phosphoric acid, therefore, is not at rest in the soil; it passes from one state of combination into another; it unites to one element for a fleeting union and quits it to unite to another element to form a union quite as ephemeral, for the agents of combination and solution contained in the soil are engaged in an incessant struggle to seize and carry away the phosphoric acid for themselves; sometimes it is the one, sometimes the other, that remove it in a transitory fashion. But the phosphoric acid retains its instability. The more intensive the culture, the more the soil is ærated, rich in humus, the more abundant the manuring with nitrate, ammoniacal and potash salts, the deeper the tilth, the heavier the crops, the less chance has the phosphoric acid in excess entrusted to the soil of passing to the soluble state, at least in large enough amount to occasion fears as to its action."

In support of these arguments Wagner relates the results he

got with experiments on basic slag on a meadow, poor in phosphoric acid, which only yielded about 1½ tons per hectare of hay (say 12 cwt. per acre). A series of plots received 800 kilos of basic slag per hectare, say 320 kilos (704 lbs.) per acre on 30 October, 1889, another series remained unmanured. As an auxiliary manure the same amount of kainit was applied and the same dose applied every year. The phosphatic manure was not renewed. The 800 kg. of basic slag per hectare (704 lb. per acre) applied once have produced :—

TABLE XLIV.—SHOWING FOR A SUCCESSION OF YEARS THE INCREASE IN HAY FROM ONE APPLICATION OF BASIC SLAG TO A POOR MEADOW.

Year.	*Increased yield.*
1890	750 kilos of hay per hectare
1891	2300 ,, ,, ,, ,, ,,
1892	2600 ,, ,, ,, ,, ,,
1893	1440 ,, ,, ,, ,, ,,
1894	2930 ,, ,, ,, ,, ,,
1895	1310 ,, ,, ,, ,, ,,
1896	1060 ,, ,, ,, ,, ,,
1897	920 ,, ,, ,, ,, ,,
1898	570 ,, ,, ,, ,, ,,
	13,880

The manuring with 800 kg. per hectare (704 lb. per acre) of basic slag, once applied, has continued to act during nine consecutive years, and has produced during this interval 13·880 metric tons of hay per hectare, say 5 tons 12 cwt. per acre. In this experiment the basic slag has not been rendered insoluble, and the reserve of manure entrusted to the soil has been nothing less than profitable. It goes without saying that this experiment, by itself alone, ought to afford instruction as to how a phosphate manure once applied behaves in its restorative action, for to entrust a soil with a reserve of manure, and to allow this manure to act for nine years without restoring the amount consumed by vegetation, would be quite irrational; moreover, the above experiments, which have been varied by others in different directions, have shown that a yearly application of manure still further increases the yield.[1]

[1] It is hardly sound or logical reasoning to apply the permanently basic slag in the soil to that of superphosphate. This meadow possibly was sour and wanted lime which basic slag supplied. Part of a 25-acre field was limed, then planted with Scots pine ; the pasture under the trees on the limed portion was easily differentiated by its excellent quality 40-50 years afterwards from the almost bare unlimed portion.—Tr.

CHAPTER VIII.

COMPOUND MANURES.[1]

Manufacture of Mixed Manures.—The manures generally used for admixture with superphosphates are Peruvian guano, bone dust, sulphate of ammonia and nitrate of soda, but the Peruvian guano dispatched from the spots of production now is much less rich in nitrogen than that imported in the past. Its place is taken by sulphate of ammonia, ground horn, dried blood, dried meat, etc. Superphosphate of potash is also prepared. The mixing is done as much as possible after the phosphate is dissolved. Mixing is not done in the dry state, except when it cannot be done otherwise.

Hand labour is the best for this kind of work. The materials, previously weighed and sifted, are made into a 2 ton heap by means of a portable box (? barrow) capable of holding 100 kilos (2 cwt.).[2] To turn the matter properly the shovel is plunged into it vertically, so as to mix it, then after having sifted it, it is made into a heap in

[1] In the wet mixing of compound manures where such things as sulphate of ammonia, meat meal, fish guano, bone meal, kainit, shoddy, etc., go up the cups, retrogradation is less marked. The other ingredients apparently, at least, retard retrogradation, if they do not prevent it to a great extent. A 30 per cent soluble phosphate which retrograded 3 to 4 per cent in a few months when dry mixed so as to give 20 per cent soluble phosphates and 7·0 per cent ammonia, maintained that composition exactly for several months in a 250 ton heap. It is better to use up superphosphates with such a marked tendency to retrograde in the making of wet mixing compound manures.—Tr.

[2] The British manure manufacturer works in cwts. to the ton, thus a very easy calculation shows that $8\frac{3}{4}$ cwts. of sulphate of ammonia (of 20·5 per cent N) to the ton mixing, gives 9 per cent of nitrogen in the mixing; a similar easy calculation shows $11\frac{1}{4}$ cwts. of superphosphate with 35 per cent of soluble phosphate to the ton mixing, gives as near as may be 19·647 per cent of soluble phosphate in the mixing, and 19·647 of soluble phosphate is equal to 9 per cent of soluble phosphoric acid (9 × 2·183).

It is all very well for the author to say inert ingredients should not be used, but it is often impossible to avoid the use of gypsum, the more so as it dries the manure and gets the core through the screen. To get the core in this case through the screen with bone dust would be a waste of money, as apparently no value is attached to insoluble phosphate. Supposing the superphosphate used tests in this case 38 per cent of soluble phosphate, it is a clear case for the addition of gypsum instead of using two grades of superphosphate. Moreover, a manure of this nature with neither potash nor bone meal would have no backbone.—Tr.

the inverse order, that is to say, by lifting it from the ground to throw on to the middle of the heap.[1]

These manipulations are sometimes rather unpleasant, such as the disengagement of dust, etc., nevertheless they form the best method of mixing. The materials so mixed are afterwards passed through a Carr's disintegrator or through the toothed crusher and a very homogeneous mixture is thus obtained. Inert materials should be avoided in these mixings. By mixing high strength superphosphates with low strength superphosphates common sorts can be made without recourse to inert materials, sand, plaster, etc.

[*Superphosphate of Ammonia* [2]] *Ammoniated Superphosphate.*—Although the composition of this manure is very variable, the most usual strength being 9 × 9, 5 × 10, or 6 × 12, the first figure indicating the percentage of nitrogen, the second the percentage of soluble phosphoric acid, this manure is in great esteem. It is analogous to dissolved Peruvian guano to which farmers are accustomed. It, moreover, presents this advantage, that its acid retrogrades less easily in the soil than that of pure superphosphate, seeing that the sulphuric acid combines first with the bases which it encounters in arable land. The mixture of superphosphate with sulphate of ammonia is easily made. Sulphate of ammonia is delivered in a finely ground granular condition. It contains 24·5 per

[1] This explanation is not very intelligible; possibly the following will make it plainer :—

Take a 10 ton mixing according to the following formula :—

	Tons.	*Cwts.*
15 cwt. superphosphate	= 7	10
3 cwt. sulphate of ammonia	= 1	10
1 cwt. bone meal	=	10
1 cwt. muriate of potash	=	10

First of all the 7½ tons of superphosphate would be laid down in a heap and accurately levelled, then the 1½ tons of sulphate of ammonia would be spread uniformly over the levelled top of the heap, then the ½ ton of bone meal uniformly over that, then the muriate over that. Then a screen with two men would be placed at one end of it and a man to get the stuff for them, that is by digging down the heap vertically and mixing it for the two men to shovel it through a ½ inch or 1 inch screen. When this first screening is done the material is screened through in the reverse direction, but this time through a ¼ inch sieve. If the heap has been laid down anything like proportionately and uniformly, samples taken from any point will agree in analysis in a manner that those who have not seen it done would hardly credit. If the 7½ tons of superphosphate were taken from the superphosphate heap, if the foreman has a good eye for bulk and weight there need be no necessity to weigh the 7½ tons; he can tell to a nicety its bulk.—Tr.

[2] This name as used by the author is misleading, applied as it is to a mere mechanical mixture of sulphate of ammonia and superphosphate of lime, and would not pass muster in a court of law in Great Britain. The translator has altered it to ammoniated superphosphate. Superphosphate of ammonia seems to imply that it is a superphosphate of lime in which the lime is replaced by ammonia. But that does not occur until the manure is dissolved by the moisture in the soil.—Tr.

cent NH3 = 20·2 per cent N and about 1 per cent moisture, which is an advantage for the manufacturer, for the mixtures 9 × 9 have to be delivered with a maximum of 6 to 7 per cent of moisture, those of 5 × 10 with a maximum of 8 to 9 of moisture, if it be not desired to be exposed to annoyances by the formation of lumps (? loose caking in the sacks). To obtain very homogeneous superphosphate of ammonia (ammoniated superphosphate) the sulphate of ammonia is added during the "dissolving" of the superphosphate by dissolving this salt in the sulphuric acid used to decompose the superphosphate, but this method of proceeding is not applicable except with small amounts of sulphate of ammonia.[1]

The process generally used in making "superphosphate of ammonia" (or ammoniated superphosphate) is as follows. The dry superphosphate of ammonia delivered in 10 ton wagons, being stored and analysed, the amount of superphosphate and sulphate required to give a mixture of 9 × 9 has to be calculated. Suppose that the sulphate of ammonia contains 20·5 N, then 20·5 kg. correspond to 100 kg. $(NH_4)_2SO_4$, 9 kg. correspond therefore to $\frac{100 \times 9}{20{\cdot}5} = 42$ kg. $(NH_4)_2SO_4$. There remains then for the superphosphate 100 – 42 = 58 kg. These 58 kg. of superphosphate must contain 9 kg. of soluble phosphoric acid, which corresponds to $\frac{100 \times 9}{58t} = 15{\cdot}5$ per cent of phosphoric acid. To make the mixture the 10 metric tons of sulphate of ammonia are laid in a heap 33 ft. long and on each heap the necessary portion of superphosphate to the total of 12·777 metric tons. Two labourers mix the two with the shovel, making the whole into one heap and recommence the same in an inverse direction. The mixer is then passed through Carr's disintegrator or the toothed crusher, then it is laid on a big heap in the warehouse for the ingredients to combine.[2]

Mixtures of superphosphate and sulphate of ammonia exhibit phenomena of a peculiar nature. They gradually heat and become damp to the touch; they dry again, and owing to the formation of gypsum, they harden more and more. The reaction lasts for a variable time. It depends on the nature of the superphosphate and

[1] Quite so, but there is no necessity to actually mix the ammonia with the acid before running the latter into the mixer. The sulphate can go up the cups like other ingredients, and precede the other ingredients if the man in charge fancies that style of mixing. The translator, however, has no great faith in the solvent action of sulphuric acid after it has been so far converted into an acid sulphate of ammonia. He prefers to send the sulphate up the cups last, after the acid has done all the work it is intended to do.—Tr.

[2] A disintegrator, whether Carr's or any other make, has its use in manure factories, but it is not at all necessary to resort to it on every occasion and to put all the manure made in the factory through it without rhyme or reason.—Tr.

its manner of manufacture, and may end in fifteen days, when the mass is in a large heap and exposed to a certain pressure. "Superphosphate of ammonia" (ammoniated superphosphate) forms a hard, sometimes rocky mass, the shifting of which is expensive, for one is obliged to blow it up with gunpowder (!!!).[1] It is crushed by Carr's disintegrator, is passed through the sieve, and bagged up immediately afterwards, for it does not solidify again if made according to rules, that is to say, if each grain of sulphate of ammonia is united to its grain of superphosphate to form a sulphophosphate. To diminish the hardening as much as possible, sand, or better still, powdered peat, sawdust, wool dust (? scutch), or chimney soot are added, and in the second place, immediate saturation of the sulphate of lime by the addition of a little water. The second grinding is therefore necessary to effect the perfect mixing of the two ingredients. In fact, if the substance be analyzed after the first crushing, there will be found 8·8 per cent of phosphoric acid and 9·2 per cent of nitrogen, together 18 per cent, but after the second crushing the product uniformly shows 9 per cent of phosphoric acid and 9 per cent of nitrogen. This method of preparation serves, equally, for all the mixing it is desired to make superphosphate of ammonia 5 × 10. For 100 kg. of mixture, take $\frac{100 \times 5}{20{\cdot}5} = 24{\cdot}4$ kg. of sulphate of ammonia of 20·5 per cent N, and consequently 75·6 kg. of superphosphate containing $\frac{100 \times 10}{75{\cdot}6} = 13{\cdot}2$ per cent. phosphoric acid. If it be a case of a wagon of 10 tons of sulphate of ammonia, 41 tons of the mixture will be obtained of the 5 × 10 mixture, requiring consequently 31 tons of superphosphate. It is easy to bring the superphosphate to the right strength by mixing a high strength superphosphate with a low strength superphosphate or with gypsum free from iron, alumina, and carbonate of lime, a poor superphosphate with a rich superphosphate, or with a double superphosphate.

[1] In the hardening of the author's so-called superphosphate of ammonia he seems to confuse mixing operations by the wet way with those by the dry way. It is perfectly feasible that through bad manipulation a mixing might so harden in the "dens" that it might almost require blasting operations to break it up, but only through culpable, nay wilful, neglect on the part of the man in charge of the mixer in not running in the proper amount of acid. Bone meal and sulphate of ammonia give a very hard glutinous mixing when sent up the cups, but sulphate of ammonia and phosphate alone should do no such thing. The translator has made numerous dry mixings of superphosphate with sulphate of ammonia in all proportions and never found the hardening to go further than caking, but he always made a point of having at least 1 cwt. to 1½ cwts. or even 2 cwts. to the ton of bone meal in such mixings, and this kept it friable and open, and when the stimulant elements of the manure had done their work then the plant had something to fall back upon.—Tr.

TABLE XLV.—NUMBER OF CWTS. REQUIRED IN A 5 TON MIXING, OR OF TONS IN A 100 TON MIXING OF A SUPERPHOSPHATE OF A GIVEN STRENGTH IN P_2O_5 TO PRODUCE A MANURE OF A GIVEN STRENGTH IN P_2O_5.

P_2O_5 in the Superphosphate.	P_2O_5 in the Mixture.											
	8·8	8·9	9·0	9·8	9·9	10·0	11·8	11·9	12·0	14·8	14·9	15·0
15·1	58·28	58·93	59·60	64·89	65·5	66·22	78·14	78·79	79·47			
15·2	57·90	58·56	59·21	64·68	65·13	65·95	77·64	78·29	78·96			
15·3	57·71	58·17	58·62	64·04	64·71	65·36	77·13	77·76	78·45			
15·4	57·15	57·80	58·43	63·63	64·28	64·94	76·63	77·27	77·93			
15·5	56·78	57·42	58·06	63·23	63·87	64·52	76·14	76·78	77·43			
15·6	56·41	57·06	57·69	62·82	63·46	64·10	75·65	76·28	76·93			
15·7	56·06	56·69	57·32	62·41	63·05	63·69	75·16	75·78	76·43			
15·8	55·69	56·32	56·96	62·01	62·65	63·28	74·67	75·30	75·97			
15·9	55·35	55·98	56·59	61·63	62·26	62·90	74·22	74·84	75·48			
16·0	55·06	55·63	56·24	61·25	61·87	62·50	73·75	74·37	75·01			
16·1	54·67	55·29	55·90	60·87	61·49	62·12	73·30	73·91	74·54			
16·2	54·33	54·99	55·55	60 49	61·10	61·73	72·85	73·45	74·08			
16·3	53·99	54·61	55·21	60·12	60·73	61·35	72·40	73·00	73·62			
16·4	53·67	54·28	54·88	59·75	60·37	60·98	71·96	72·56	73·18			
16·5	53·33	53·94	54·54	59·38	59·99	60·60	71·52	72·11	72·73			
16·6	53·02	53·62	54·21	59·03	59·64	60·24	71·09	71·68	72·30			
16·7	52·70	53·30	53·89	58·68	59·28	59·88	70·66	71·25	71·86			
16·8	52·38	52·98	53·57	58·33	58·92	59·53	70·25	70·81	71·44			
16·9	52·07	52·66	53·25	57·98	58·55	59·17	69·72	70·41	71·01			
17·0	51·77	52·36	52·94	57·65	58·24	58·83	69·42	70·00	70·60			
17·1	51·46	52·05	52·62	57·31	57·89	58·48	69·01	69·58	70·18			
17·2	51·17	51·75	52·32	56·98	57·55	58·15	68·61	69·18	69·77	86·06	86·64	87·22
17·3	50·88	51·45	52·02	56·65	57·23	57·81	68·22	68·79	69·37	85·57	86·14	86·72
17·4	50·58	51·16	51·72	56·32	56·90	57·48	67·82	68·39	68·98	85·07	85·65	86·22
17·5	50·29	50·87	51·42	56·01	56·57	57·15	67·44	68·00	68·58	84·59	85·15	85·72
17·6	50·05	50·58	51·23	55·68	56·24	56·82	67·05	67·61	68·19	84·10	84·67	85·23
17·7	49·72	50·28	50·84	55·37	55·93	56·49	66·67	67·22	67·79	83·62	84·18	84·74
17·8	49·44	50·00	50·56	55·05	55·62	56·18	66·30	66·84	67·42	83·16	83·71	84·28
17·9	49·16	49·72	50·27	54·74	55·30	55·86	65·92	66·46	67·04	82·68	83·24	83·79
18·0	48·89	46·44	49·89	54·44	54·99	55·55	65·55	66·10	66·67	82·22	82·77	83·33
18·1	48·62	49·17	49·72	54·14	54·69	55·25	65·19	65·73	66·30	81·77	82·31	82·87
18·2	48·35	48·90	49·44	53·84	54·39	54·94	64·83	65·37	65·94	81·32	81·87	82·41
18·3	48·08	48·63	49·17	53·55	54·09	54·64	64·48	65·01	65·57	80·87	81·41	81·96
18·4	47·83	48·38	48·91	53·26	53·80	54·36	64·13	64·68	65·22	80·44	80·97	81·53
18·5	47·56	48·10	48·64	52·97	53·51	54·05	63·78	64·31	64·86	80·00	80·54	81·08
18·6	47·32	47·85	48·39	52·69	53·22	53·76	63·45	63·97	64·52	79·58	80·11	80·66
18·7	47·07	47·60	48·12	52·41	52·94	53·48	63·11	63·63	64·18	79·16	79·69	80·23
18·8	46·80	47·34	47·86	52·12	52·65	53·19	62·76	63·28	63·83	78·78	79·25	79·79
18·9	46·50	47·09	47·61	51·84	52·37	52·90	62·43	62·95	63·49	78·30	78·83	79·36

Superphosphate of Ammonia and Potash.[1]—This (a mechanical mixture of sulphate of ammonia and potash salts) is prepared in

[1] This also is a name which would not pass muster in Great Britain, implying as it does that it is superphosphate of lime in which the lime has

the same way. Suppose it is desired to prepare a mixture of this nature with 5 per cent of nitrogen, 7·5 per cent of potash, and 9 per cent of phosphoric acid, and that there was to be used for the purpose sulphate of ammonia with 20·5 N, and potash salts with 37 per cent K. To get 100 kg. of superphosphate of ammonia and potash it is therefore necessary to use :—

$$\frac{100 \times 5}{20{\cdot}5} = 24{\cdot}4 \text{ kg. of sulphate of ammonia.}$$

$$\frac{100 \times 7{\cdot}5}{37{\cdot}0} = 20{\cdot}3 \text{ kg. of potash salt, and consequently}$$

55·3 kg. of superphosphate testing.

$$\frac{100 \times 9}{55{\cdot}3} = 16{\cdot}27 \text{ per cent of phosphoric acid.}$$

Ten tons of the sulphate of ammonia used would therefore give 41 tons of the compound manure. It would thus be necessary to use 31 tons of potash salt plus superphosphate, say 8·32 tons of the first, and 22·680 of the second. These manure mixtures find an outlet chiefly in regions where the vine, tobacco, the hop, and vegetables for preserves are cultivated. They are likewise esteemed for the culture of the sugar beet, barley, and potatoes. Mixtures of superphosphate and potash salts become readily moist in the store, so that they cannot be prepared a long time in advance. The use of calcined salts prepared from the waste of potash factories, have the drawback that they nearly always contain magnesium chloride. When they are dried with precaution at 100° C., they are exempt from basic magnesium compounds. The retrogradation of the soluble phosphoric acid in mixed manures under the action of the basic salts of potash, have been studied by Emmerling as a result of experiments thereon. By treating salts of potash in the reverberatory furnace to partial fusion, about 800° C. (1472° F.), the magnesium chloride which they contain is decomposed in the moist condition as follows :—

$$MgCl_2 + H_2O = MgOHCl + HCl$$

According to the equation—

$$CaH_4(PO_4)^2 + MgO = CaMgH_2(PO_4)^2 + H_2O,$$

a molecule of magnesia can retrograde a molecule of phosphoric acid, from which it follows that one part of MgO can render 3·55 per cent of phosphoric acid insoluble. If one use, for example, twenty-

been chemically replaced by equivalent proportions of ammonia and potash, whereas it is a mere mechanical mixture of superphosphate with sulphate of ammonia and potash salts.—Tr.

nine parts of potash salts with 2·05 per cent of free magnesia (percentage controlled by estimation), the $\frac{2 \times 0{\cdot}5 \times 29}{100} = 0{\cdot}59$ part MgO suffices to combine $0{\cdot}59 \times 3{\cdot}55 = 2$ parts of phosphoric acid; as an actual fact, only 1·4 of insoluble was obtained, which proves that the magnesia did not exert all its action. The cause lies in the slight solubility of magnesia, and in the fact that the salts of potash combine partially with the precipitate formed, so that a part of the phosphoric acid of this latter remains in solution.

Nitrophosphate.—The use of nitrate of soda in compound manures is rather restricted; it is used in making nitrophosphate, sometimes in nitrophosphate of ammonia. It is found that nitrate of soda and sulphate of ammonia are incompatible, and that in fact it is better to use these manures separately. Besides, mixtures of superphosphate and nitrate sometimes enter into spontaneous combustion in the bags.[1] The mixtures of superphosphate and nitrate must be dry mixing. They are no longer objects of terror to the manufacturer, provided that the superphosphate used has been properly made, for dry nitrate of high percentage mixed with a superphosphate, likewise dry, does not give off nitric acid and cause loss of nitrogen as was often the case formerly when superphosphates were wet and the nitrates charged with chloride of sodium. The sodium chloride decomposed by the free phosphoric acid caused the bags to burst in transit, for there is no substance which rots bags like free chlorine and fluorine, two elements given off when nitrate and damp superphosphates are mixed.

Finally, a manure is made for meadows by mixing kainit with superphosphate or with basic slag.[2] The mixing entails no difficulty. The ingredients are mixed with a shovel, then the heap is turned over, the product perhaps passed immediately to the centrifugal crusher, then to the sifting machine. If the kainit be in blocks or lumps it must be passed to the crusher to reduce it to the desired fineness.

It has already been remarked that in the case of the superphosphate of ammonia of high strength, the phosphoric acid soluble in water did not retrograde even when the superphosphate entering

[1] When manure containing nitrate takes fire spontaneously in the bags it is not a case of damp or wet superphosphate, nor is it a case of impure nitrate; but it is due wholly and solely to the superphosphate fresh from the mixing "den" being mixed with the nitrate and bagged up before it has had time to cool. Cold superphosphate, however damp, does not act on nitrate of soda, unless in very warm weather.—Tr.

[2] Kainit long in stock is generally so damp that it blocks and chokes up the crusher. The only way to grind it is by hand labour, by the aid of wooden mallets with long arms, and it is altogether a costly piece of work. Kainit should not be stored in sacks but in bulk on a concrete floor where the water can drain away from it.—Tr.

into the mixture was of such a nature as to readily lend itself to retrogradation. The causes of this phenomena are of both a physical and chemical nature. The more the superphosphate is distended by ballast, which is here sulphate of ammonia, the more distant the particles are from one another and preserve their condition. From a chemical point of view, sulphate of ammonia possesses the property of hindering the basic sesquioxides from precipitating themselves, but it is clear that a retrograded superphosphate cannot be improved by mixture with sulphate of ammonia.

Tables for the Calculation of Superphosphates of Ammonia.—The first vertical column of Table I gives the content of sulphate of ammonia in per cents of nitrogen, from one-tenth to the next tenth within the limits which are generally met with in practice. The top horizontal column contains the usual percentages in nitrogen of "superphosphates of ammonia," say 2, 3, 4, 5, 6, 7, 8, 9 per cent of nitrogen. The figures contained at the points of intersection of these vertical and horizontal columns show the number of cwts. of sulphate of ammonia that must be added to the heaps to get 100 cwts. of the mixture with the desired nitrogen content. Thus, for example, to get a superphosphate of 5 × 10, with 4·9 per cent of nitrogen from a sulphate of ammonia, of 20·2 per cent of nitrogen, it is necessary to add for 100 cwts. of mixture sand (!) and superphosphate, including 24 to 25 cwts. of sulphate of ammonia. Table II gives corresponding values for calculating the superphosphates.

TABLE XLVI.—SHOWING IN CWTS. THE AMOUNT OF SULPHATE OF AMMONIA OF DIFFERENT STRENGTHS THAT MUST BE CONTAINED IN A 5 TON HEAP TO GET A MANURE CONTAINING FROM 1·850 UP TO 5 PER CENT NITROGEN.

Per cent N	1·85	1·90	1·95	20·0	2·85	2·90	2·95	3·0
19·5	9·49	9·74	10·00	10·26	14·62	14·87	15·13	15·38
19·6	9·44	9·69	9·95	19·21	14·54	14·79	15·05	15·31
19·7	9·40	9·65	9·90	10·15	14·46	14·72	14·97	15·23
19·8	9·34	9·69	9·85	10·10	14·39	14·64	14·89	15·15
19·9	9·30	9·55	9·80	10·05	14·32	14·57	14 82	15·08
20·0	9·25	9·50	9·75	10·00	14·25	14·50	14·75	15·00
20·1	9·20	9·45	9·70	9·95	14·18	14·43	14·68	14·92
20·2	9·16	9·41	9·65	9·90	14·10	14·35	14·60	14·85
20·3	9·11	9·36	9·61	9·89	14·04	14·29	14·53	14·78
20·4	9·67	9·30	9·56	9·80	13·97	14·22	14·46	14·71
20·5	9·02	9·27	9·51	9·75	13 90	14·15	14·42	14·63
20·6	8·98	9·22	9·47	9·71	13·83	14·08	14·32	14·56
20·7	8·94	9·18	9·42	9·66	13·77	14·01	14·25	14·50

Per cent N	3·85	3·90	3·95	4·0	4·85	4·90	4·95	5·00
19·5	19·74	20·00	20·26	20·51	24·87	25·13	25·39	25·64
19·6	19·64	19·90	21·5	20·41	24·74	25·00	25·25	25·51
19·7	19·54	19·80	20·04	20·31	24·61	24·87	25·13	25·38
19·8	19·45	19·70	19·95	20·20	24·49	24·75	25·00	25·25
19·9	19·35	19·60	19·85	20·10	24·36	24·62	24·87	25·13
20·0	19·25	19·50	19·75	20·0	24·25	24·50	24·75	25·00
20·1	19·15	19·40	19·65	19·90	24·13	24·38	24·62	24·88
20·2	19·05	19·31	19·55	19·80	24·01	24·25	24·50	24·75
20·3	18·97	19·22	19·45	19·71	23·89	24·14	24·39	24·63
20·4	18·88	19·12	19·30	19·61	23·78	24·02	24·27	24·51
20·5	18·78	19·02	19·27	19·51	23·65	23·90	24·14	24·39
20·6	18·69	18·93	19·17	19·42	23·54	23·79	24·03	24·28
20·7	18·60	18·84	19·08	19·32	23·43	23·67	23·91	24·15

CHAPTER IX.

THE MANUFACTURE OF PHOSPHORIC ACID, DOUBLE SUPERPHOSPHATES, AND VARIOUS PRODUCTS.

Historical Review.—The manufacture of phosphoric acid has lost much of its former importance. The market for raw materials and finished products constitutes one of the most important factors in the development of an industry. Formerly, when pure phosphates of high strength were rare, whilst phosphates of low strength abounded, the phosphoric acid industry and its derivatives were in an excellent condition for living and prospering. The extensive deposits of phosphorite in Germany induced manufacturers to devote themselves to the manufacture of a product which, separated from the impurities which accompany it in the raw material, was admirably adapted for the manufacture of one of the most esteemed manures, which is the double superphosphate. The discovery of the Lahn phosphorite beds took place at the same epoch as the Strassfurt deposits of potash salts, when Liebig had just formulated his mineral manure theory. Lahn phosphorite, which, as is known, contains a large proportion of iron and alumina, was received with open hands by manufacturers, but great was their astonishment when they realized that this material was absolutely unfit for superphosphate manufacture. Dissolved by sulphuric acid, it yielded a product, the soluble phosphoric acid content of which, already low enough, diminished still further in such great proportions, owing to retrogradation, that superphosphate manufacturers had to abandon its use. Two large chemical factories, which owned a great part of the Lahn phosphorite deposits, tried to utilize the material in phosphoric acid manufacture.

The fundamental idea of the process of manufacture is contained in Graham's method of analysis. It consists in digesting the pulverized phosphate with 5 per cent sulphuric acid, in titrating the dissolved phosphoric acid by uranium solution, leaving the oxide of iron intact. The principle of the process is thus represented by the following equation :—

$$\underset{310}{Ca_3(PO_4)^2} + \underbrace{\underset{294}{3H_2SO_4}}_{604} = \underbrace{\underset{408}{3CaSO_4} + \underset{196}{2H_3PO_4}}_{604}$$

By a strange coincidence, the old manuals state that by treating tricalcic phosphate with dilute sulphuric acid, monocalcic phosphate is obtained. Now this statement is erroneous because, as will be seen further on, only a small amount of phosphoric acid enters into solution. But even by using sulphuric in insufficient amount like that calculated for the preparation of monocalcic phosphate, free phosphoric acid is obtained seeing that a part of the $Ca_3(PO_4)^2$ remains undecomposed. As far back as 1870, the firm of H. & E. Albrecht at Biebrich, installed an experimental factory for the manufacture of phosphoric acid, but the affair turned out badly because at that time suitable appliances for separating the phosphoric acid from its insoluble residue were not in existence. It was only by the use of the filter press already known at that time in sugar works, that the manufacture of phosphoric acid became lucrative, for the conversion of dilute phosphoric acid into double superphosphates did not in the beginning present insurmountable difficulties. Now this double superphosphate—with a minimum of 40 per cent P_2O_5—soon became in very great demand, as much by agriculturists as by manure manufacturers, to whom it afforded a simple and easy means of securing a high percentage of P_2O_5. But let us examine the manufacture of phosphoric acid a little more closely.

Manufacture of Phosphoric Acid.—A 50 per cent phosphate ($Ca_3P_2O_8$) is used. If damp, it is dried on metal plates. If lumpy the lumps are crushed by a jaw-breaker and then reduced to the requisite fineness by a flatstone mill or a ball mill. The ground phosphate is then fed into the vats by a chain elevator, 1 to 2 tons per charge; the sulphuric acid and the necessary water (wash water containing P_2O_5) to dilute the acid to 16° B., is run in at the same time. The charging of the vats lasts twenty minutes, and during this time decomposition is completely effected, the phosphoric acid is liberated, the sulphuric acid has taken its place and combined with the lime to form gypsum, which has to be separated from the liquid. For this purpose the muddy liquids from the decomposition vats are collected in a collecting tank lower down, fitted with an agitator, its rôle is to maintain the solid particles in suspension until the mixture is forced to the filter presses by a membrane pump, in which the acid liquid alone comes in contact with rubber or lead. The filter presses used have 50 plates, and are capable of treating 14 tons of phosphate in twenty-four hours (say three tons P_2O_5). The filter plates are of pitch-pine, the frames are of the same wood or of oak. The gutters are of plum-tree wood. When the filter press is charged, its contents are washed with water under

pressure until the liquid which flows away only tests 0·25° B., a density equal to that of gypsum-saturated water. The wash water then contains on an average 3 per cent P_2O_5; it is used, as already seen, to reduce the sulphuric acid to 16° B. The phosphoric acid collected in a "weak solution" tank tests about 12° B., say about 4° B. less than the sulphuric acid used; there is reason to conclude that a part of the latter has combined with the lime present in the phosphate as $CaCO_3CaFl_2$, $CaSiO_3$. A weak phosphoric acid solution of average quality has the following composition:—

	Per cent.
P_2O_5	8·0
SO_3	0·2
CaO	0·4
$(FeAl)_2O_3$	0·3

and small quantities of HF, Si, MgO, etc. For most applications, especially for the manufacture of double superphosphates, the phosphoric acid must be concentrated to a certain extent. It was at first attempted to concentrate it by evaporation by lead steam coils, but the pipes became rapidly incrusted with lead salts and lost their conductivity. This process was therefore abandoned, and attempts made to concentrate the acid by bottom heat. Great flame ovens were constructed heated by combustion gases. These gases are led underneath the liquid contained in a pan surmounted by an arch. The pan is of strong wrought-iron, lined inside with stones which resist acid, and thus was protected from direct contact with the flame and the phosphoric acid. On the other hand, the exterior side of the pan is naked. The dilute solution of phosphoric acid runs in continuously in the back part of the pan, until after two or three days an average concentration of 50° B. is obtained. The concentration is then finished and the phosphoric acid, making 56° to 58° B., is finally run out by a central gutter, whilst the contents of the pan are continuously agitated so that no mud remains. It is collected in wooden vats, or in lead-lined iron ones. In this condition the phosphoric acid is turbid and blackish owing to the presence of soot deposited by the combustion gases. It contains about 54 per cent P_2O_5, 1·5 per cent of $FeAl_2O_3$, and variable amounts of gypsum, phosphate of lime, calcium fluoride, hydro-fluosilicic acid, arsenic, etc.

Up to 1890, the factory of H. & E. Albrecht treated about 60 tons of phosphate in twenty-four hours. Five large evaporation ovens, analogous to those described, were installed, which evaporated the enormous amount of 200 tons of water in twenty-four hours. The largest of these evaporation pans was 16·5 metres (say 54 feet) long, and 5·5 metres (say 18 feet) wide, but it was divided into two compartments by a longitudinal diaphragm. It had a capacity of 36 cubic metres, and yielded at one operation 55·8 tons of 54 per

cent phosphoric acid, vaporizing 270 tons of water with an expense of 349 tons of coal, 100 kg. (220 lb.) of coal vaporized, 770 litres (1694 lb.) of water (say 1 lb. of coal furnished nearly 8 lb. of steam), and yielded 160 kg. (352 lb.) of concentrated phosphoric acid. The evaporation was at the rate of 1626 litres (say $32\frac{1}{2}$ cwt.) per hour.

The ovens installed at the Wetzlar factory were not so big. When the acid was brought to the desired density it sometimes happened, owing to want of supervision, that in the parts of the pan most exposed to the heat the phosphoric acid was evaporated to dryness, and vitreous lumps of a greyish-blue colour, partially diaphanous, formed. The analysis of this vitreous mass was very difficult, because it was impossible to dissolve it by ordinary methods. Prof. Krantt, of Hanover, succeeded in dissolving it, by heating it with borax; the analysis gave 70 per cent of P_2O_5, besides alumina, iron, lime, alkali, and hydrofluoric acid; silica, supposed to be present in large amount, looking to the vitreous nature of the mass, was only found in traces combined with fluorine. The substance thus consisted chiefly of metaphosphate. In the evaporation of the phosphoric acid, the steam entrains a great part of the dissolved HF and H_2SiF_6.

Manufacture of Double Superphosphate.—The greater part of the phosphoric acid so produced was used in the manufacture of double superphosphates. This manufacture is distinguished from ordinary superphosphate manufacture by the fact that phosphoric acid is substituted for the sulphuric acid. The phosphate is then rendered soluble according to the following equation :—

$$\underbrace{Ca_3(PO_4)_2}_{310} + \underbrace{4H_3PO_4}_{392} = \underbrace{3CaH_4(PO_4)_2}_{702}$$

$$\underbrace{\qquad\qquad\qquad}_{702}$$

It is clear that in actual practice the method of conversion is not so simple, because phosphates containing all manner of impurities are used, and the nature of the phosphoric acid, as well as that of the superphosphate, plays a preponderant rôle. The phosphates which are the most easily dissolved by phosphoric acid, are sandy phosphates with a high percentage of carbonate of lime, such as Somme phosphate and Malogne phosphate. This phosphate is mixed in the proportion of 1 ton to 4 tons of 54 per cent phosphoric acid. This mixing is done in the same manner, and with the plant, as that in which the phosphate is dissolved by sulphuric acid. To elevate the concentrated phosphoric acid and bring it to the mixing apparatus, either a membrane pump, a centrifugal pump, or an injector is used. The first of these pumps is sure in its working and can elevate the acid to any desired height; the second, which lends itself more particularly to the elevation of dilute phosphoric acid, is liable to stop working when the acid is concentrated or

muddy ; injectors are the most convenient, but it must be remembered that they dilute the acid 1° to 2° B.[1]

The principal difference which exists between double superphosphate and ordinary superphosphate lies in the fact that the latter is a mixture of monocalcic phosphate and gypsum, whilst double superphosphate only contains as impurities a few per cents of gypsum, and forms essentially a monocalcic phosphate containing free phosphoric acid in excess. That is why double superphosphate is less easily dried than ordinary superphosphate, and must therefore be very carefully dried by artificial means.

The process of manufacture just described appears very simple ; it none the less requires the control of a good chemist, the more so as the raw material used is always contaminated with impurities. The following example will show what field of action is here open to the chemist. Wetzlar's factory, of which the daily production of double superphosphate was about 12 tons, made a product in 1883 containing 34 per cent P_2O_5 soluble in water and 13 per cent P_2O_5 insoluble in water ; two years afterwards the P_2O_5 soluble in water had risen to 43 to 45 per cent with 3·6 insoluble in water. 100 kg. of phosphoric acid in the merchandise consisted therefore—

In 1883 of 72·3 [$34 \times 100 \div 47$] of phosphoric acid soluble in water.

In 1885 of 90·8 [$45 \times 100 \div 48$] per cent phosphoric acid soluble in water.

As at that time phosphoric acid soluble in water was valued at 0·65 francs the kg., whilst insoluble in acid was not generally paid for at all, the above improvement represents an increase in profit of £25 per day without taking into account the other advantages attached to the improvement in the working. The capital point in the manufacture of phosphoric acid is to dissolve the least possible amount of sesquioxides $(FeAl)_2O_3$, because it is to their presence in superphosphate that its retrogradation is due. It is clear also that the phosphates ought to be exhausted as completely as possible to reduce the expenditure of sulphuric acid to the minimum and to have the least impurities, lime, hydrofluoric acid, etc., in the weak solutions. Up to 1884, it was believed that the longer the action was prolonged in the mixing tank, the more complete was the extraction of the phosphoric acid. It was further believed that a temperature of 60° to 80° C. or 140° C. (176° F.) was necessary, or was at least conducive to the progress of the operation. Thus the acid and the water were mixed in the mixing vat, and the heat of the reaction brought the temperature of the mixture to 70° C. (158° F.);

[1] It is difficult to see why the ordinary appliances for raising sulphuric acid in manure works cannot be used, viz. the ordinary "montejus," sometimes called the egg or air vessel. This air vessel is filled with acid by a syphon from a tank alongside. When full, air is pumped into it by one pipe and the acid rises from it up another pipe into the ten ton store tank overhead. Any hitch with the pumps described by the author mean of course the stoppage of the mixing when the store tank is empty. The air vessel with ordinary attention gives no trouble.—Tr.

the phosphate was then run in and the agitator was wrought for two to three hours. But that was bad working. Systematic manufacturing tests have led to the following conclusions :—

1. The percentage of sesquioxides in the weak solution increases with the length of the agitation and with the rise of temperature, and the other impurities behave in the same way, HF, H_2SiF_6, CaO.

2. The percentage of phosphoric acid in the insoluble residue is least when the agitation only lasts about twenty minutes, from that time onwards it decreases with the duration of the agitation, but in proportion to the oxide of iron content. There would appear to be a retrogradation of the free phosphoric acid, dissolved under the influence of the oxide of iron, as in superphosphates.

3. The expenditure of sulphuric acid increases with the duration of the agitation and the elevation of the temperature. Under opposite conditions, the sulphuric acid content of the "weak solutions" naturally decreases. These experiments were made in course of manufacture from Lahn phosphorite; afterwards they were generalized, especially for verifying the facts pointed out in 1 and 3, which are likewise applicable to Liége phosphate. The results thus ascertained were applied immediately in industrial practice. To diminish the duration of the mixing process was easily done : to lower the temperature of the mixing during working, the sulphuric acid was diluted with the wash water and the hot dilute acid passed through a tubular condenser, cooled by circulation of water ; finally, to decompose the phosphate by sulphuric acid, half quantities were taken. Great advantage arises from this style of working, less handling, abolition of night work by installing of new filter presses, economy of sulphuric acid, more complete extraction of the phosphoric acid from the phosphates, longer life of the filter cloths, and above all, obtaining a product richer in phosphoric acid soluble in water. This product then had the following composition :—

TABLE XLVII.—SHOWING THE ANALYSIS OF DOUBLE SUPERPHOSPHATE.

	Per cent.	
Monocalcic phosphate $CaH_4(PO_4)_2$	60·0	
Free phosphoric acid H_3PO_4	9·5	
Dicalcic phosphate $Ca_2H_2(PO_4)_2$	4·5	
Tribasic phosphate $C_3(PO_4)_2$	2·0	48·1 per cent of total P_2O_5.
Phosphate of iron and alumina $(FeAl)PO_4$	4·0	43·3 per cent of P_2O_5 soluble in water.
Hydrated sulphate of lime $CaSO_4 2H_2O$	5·0	
Magnesia, silica, fluorine	2·0	
Sand, etc.	4·0	
Moisture	9·0	
	100·0	

But all the manufacturing problems were not solved. An important point is the exact determination of the amount of sulphuric acid required to decompose the phosphate. That amount cannot be fixed, except by inference from the SO_3 in the weak solution of a preceding operation, and to determine that it is necessary to make a quantitative analysis. If a sufficient amount of acid be not used the solution contains lime in excess, and after evaporation it is often converted into a thick broth, which it is impossible to work in that condition. This drawback is remedied by introducing sulphuric acid, but it would be better not to use that expedient owing to the disengagement of hydrofluoric acid fumes. Another drawback which arises from a deficiency of sulphuric acid, is that the extraction of the phosphoric acid is incomplete. But an excess of sulphuric acid causes even greater drawbacks. In fact, if the phosphoric acid solution, with excess of sulphuric acid, be evaporated, it becomes inactive towards the phosphate which it is intended to dissolve, which is likewise the case with too concentrated sulphuric acid. The phosphate is not attacked by the acid, and the manufacturer is at his wits' end to know what to do with this dilute mixture of phosphate and phosphoric acid. At the Wetzlar factory when this mishap occurred, the phosphoric acid was absorbed by powdered peat, in the ratio of three to one; the product contained about 33 per cent of P_2O_5, and when it could not be got rid of directly, it was afterwards mixed with double superphosphate. Once finished, the percentage of phosphoric acid soluble in water was thus considerably increased, but at the expense of its physical properties.

Afterwards, a very simple way was found to restore its activity to the phosphoric acid which had become inactive. All that has to be done is to treat it with finely powdered quicklime. But phosphoric acid so treated does not behave like normal acid in the course of the work. As already stated, the residual gypsum left in the filter presses forms a very cumbersome waste product. It contains 40 to 50 per cent of water. It is run on to a heap. In summer it dries on the surface, it is then turned over with the plough, and passed through a Carr's disintegrator, and marketed as a powder. In wet years it is dried in a simple drying machine, when there is an outlet for it. This product is known in commerce as phosphatic gypsum; it contains 60 per cent of gypsum and 3 to 4 per cent of phosphoric acid, of which 1 per cent is soluble in citrate and 0·25 soluble in water. It has been tried to have this gypsum specially adopted as a preservative agent of the fertilizing principles of farmyard manure, and it has been proposed to spread it in stables, and on farmyard manure. This use is very rational, for precipitated gypsum combines very readily with the ammonium carbonate of farmyard dung. But it is clear that this material

cannot stand heavy freight charges, for its selling price is almost entirely absorbed by drying expenses and loading. It is easy to understand that to a factory which produces 100 tons of phosphatic gypsum a day, the sale of this waste is of no great importance in itself, whilst the shifting of it and its storage form a big item in the general expenses account. Thus the Wetzlar factory was forced to purchase a piece of land for 30,000 marks (£1500) for this purpose and to instal on it an aerial conveyor at a cost of 16,000 marks (£800). It has already been seen that double superphosphate must be dried artificially. The principle of this operation consists in passing over the substance a great amount of air at a uniform temperature, the degree of which depends on the superphosphate. The dryers installed at first fulfilled none of these conditions; the product obtained therefore was very unequal, one part was superheated and its phosphoric acid had partially retrograded. To improve the drying laboratory, experiments were undertaken to find the limit of temperature at which the phosphoric acid ceased to retrograde. These researches were made on Lahn double superphosphate and gave quite unexpected results. Up to 120° C. (248° F.) the content of phosphoric acid soluble in water underwent no modification, it even appreciably increased between 120° C. (248° F.) and 170° C. (338° F.), and it is only above 170° C. that the much-dreaded retrogradation occurred. At first sight one would be inclined to explain this fact in the sense that the H_3PO_4 and $Ca_2H_2(PO_4)_2$ are at a low temperature in a state of equilibrium in superphosphate, and react the one on the other at a high temperature to form $CaH_4(PO_4)_2$. It was then a question of realizing this temperature of 170° C. in actual practice. But this problem is a difficult one and does not appear to have ever been perfectly solved. It will be seen in the sequel that double superphosphate made from Liége phosphate behaves in quite a different manner; not only is there no increase in the phosphoric acid soluble in water, but retrogradation commences as soon as the drying temperature exceeds 120° C. The true cause of that difference in the behaviour of the two superphosphates has not been ascertained, but it may be concluded that each phosphate has a nature of its own, and requires to be treated in accordance therewith. It is the phosphates poor in sesquioxides which work best, such as Florida phosphate which is used in a Swedish factory. The crushing of the dried superphosphate is done in a Carr's disintegrator, like an ordinary superphosphate, and presents no difficulty. The plant required for making 7½ tons of 55 per cent phosphoric acid is the following:—

4 to 5 filter presses.

1 large and 3 small mixing vats.

2 centrifugal pumps.
3 membrane pumps.
Cooling and dilution plant.
Sulphuric acid store tank, 10 cubic metres capacity.
$\frac{35}{40}$ per cent sulphuric acid store tank, 20 cubic metres capacity.
2 sulphuric acid measuring tanks.
2 wash water tanks, 15 cubic metres capacity.
Dilute phosphoric acid tank, 40 cubic metres capacity.
Concentrated phosphoric acid tank, 10 cubic metres capacity.
Membrane pump for concentrated phosphoric acid.
Oven for drying the phosphoric acid.
Lead piping.
1 steam engine 25 H.P. with shafting.

As mentioned at the outset, the phosphoric acid industry has lost much of its importance. Of twelve large factories at work twenty years ago, there are only four or five still at work, which also make various kinds of phosphates, of which a few words will now be said.

Manufacture of Superphosphate of Potassium and Ammonium.—The oldest and the most important of the phosphoric acid derivatives is the neutral phosphate of sodium, Na_2HPO_4, which occurs in the form of beautiful monoclinic crystals consisting of 20 per cent Na_2O, 20 per cent P_2O_5 and 60 per cent of water, and can therefore be prepared easily in the pure state. The phosphate of sodium is not employed as manure, but rather the phosphate of potash and of ammonia about to be described. The manufacture of phosphates of potassium and ammonium presents no difficulties, especially that of potassium, owing to its weak crystallizing power. From that point of view, the mono-ammonium phosphate AmH_2PO_4, which is the most stable of all the phosphates of ammonia, behaves much better. It crystallizes without water of crystallization in beautiful tetragonal prisms with a pointed apex. The acid phosphates are generally very difficult to filter when they are neutralized with soda. Now, as the pure non-ammoniacal phosphate is much less used as a manure than the impure phosphate of ammonia, the manufacture of the latter furnishes a pure ammoniacal salt as a secondary product. The most simple process to manufacture phosphate of ammonia as well as sulphate of ammonia, is to use gas liquor, working with the well-known apparatus of Feldmann. The salt is not separated from the muddy precipitate obtained, which is likewise used as manure, but there forms at the surface fine crystalline efflorescences of AmH_2PO_4, which it is easy to collect apart and to purify by fresh crystallization. In order to prepare in the same manner a crude phospho-potassic manure, potash must be employed as the raw

material, but that is too dear. Nevertheless, in 1892, the Biebrich factory produced small quantities of phosphate of potash by saturation of potash by phosphoric acid, although the product was of bad quality (much insoluble P_2O_5 and H_2O).

Manufacture of Sulpho-phosphates.—During this time chemists tried new methods of manufacture. At that time Dr. Paul Wagner, 1892, published his pamphlet on the use of chemical manures in horticulture, and gave the idea of manufacturing pure and concentrated chemical manures. This idea was taken up by H. Albrecht, director of the Biebrich factory, which henceforth manufactured phosphates of potash and ammonia and nitrate by mixing the ingredients in different proportions. As a matter of fact, a sort of phosphate of potash was known as early as 1886, but its percentage of sulphuric acid rendered it unfit for the purposes to which such mixtures are applied. This product is the sulpho-phosphate of potash which was at first made by Meyer, as well as an analogous product, the sulpho-phosphate of ammonia.

The sulpho-phosphates are interesting from several points of view, and possess such valuable properties that there is reason to ask why agriculture and the chemical manure trade do not make more frequent use of them. So long as the Wetzlar factory was at work, it produced great quantities intended chiefly for export to the Dutch East Indies, but from that time they have not been heard of. If equal parts of 55 per cent phosphoric acid and of sulphate of ammonia or sulphate of potash be mixed together and heated to 80° C., the components unite, and form a dry pulverulent salt. An addition product of the two substances is formed :—

$$Am_2SO_4 + H_3PO_4 = AmHSO_4 + AmH_2PO_4$$
$$K_2SO_4 + H_3PO_4 = KHSO_4 + KH_2PO_4$$

The product contains respectively, 25 per cent P_2O_5 and 10·5 N, and 24 per cent P_2O_5 and 27 per cent K_2O. The phosphoric acid is present in a condition almost entirely soluble in water. The percentage of sulphuric acid is about 30 per cent. (Peculiar thing, an analogous compound cannot be obtained from soda in this way.) The manufacture is exceedingly simple. There is dissolved in the "weak solution," obtained in the manufacture of phosphoric acid ; an equivalent quantity of alkaline sulphate, viz. 100 Am_2SO_4 for 55 P_2O_5 and 100 K_2SO_4 for 48 P_2O_5, and the solution is evaporated until the boiling-point rises to 110° C. (230° F.) for the potash salt and 140° C. (284° F.) for the ammonia salt. Finally, the hot mass is run into a cooling beck and agitated until it solidifies. This process is much more simple and cheaper than that of making double superphosphate. It is well

to take into account the advantages which the sulpho-phosphate possesses in virtue of its acid nature. It may be used in larger quantities in calcareous and heavy soils, either alone or mixed with basic slag or powdered lime. We know that in virtue of its high lime content, basic slag can be mixed neither with ammoniacal salts nor with superphosphates, for in the first instance there would be a loss of nitrogen, and in the second of phosphoric acid soluble in water. Now, not only does the mixture of basic slag with the sulpho-phosphate of ammonia exclude losses of this nature, but it also has the effect of increasing the percentage of phosphoric acid soluble in water. According to experiments made on this subject, this increase reached 13 per cent of the total phosphoric acid in the mixture. Another advantage arising from the acid character of the sulpho-phosphates resides in the possibility of using particularly impure phosphates, such as those containing oxide of iron and alumina. It is precisely this fact which will bring the sulpho-phosphates into good repute some day, when the abundance of pure phosphates has given place to penury.

But there is a class of mineral phosphates of low content in lime, and the base of which is alumina with more or less oxide of iron. Redonda phosphate consists of important beds of this nature. These phosphates can be treated neither by the ordinary dissolving process nor by the process of extraction of the phosphoric acid, because the latter is present in a form difficult of attack. Now the manufacture of sulpho-phosphates gives us the means of profiting excellently by these phosphates, otherwise unutilizable, which explains their cheapness. The method about to be described, and which is absolutely unpublished, is based on the following equation :—

$$2AlPO_4 + AmHSO_4 + H_2SO_4 = Al_2(SO_4)^3 + 2AmHSO_4,AmH_2PO_4$$

The ground phosphate is fused at a temperature of 120° to 140° C. with super acid ammonium bisulphate. The duration of this operation depends on the degree of resistance of the substance. Most often it requires two to three hours. It is clear that the water evaporated in that time must be replaced. The phosphate is dissolved much more rapidly and more completely when done under pressure and at an elevated temperature. The plant required by that style of working is certainly more costly, but the work would be done better and factory expenses run less.

The product so obtained is a sulpho-phosphate of ammonia and sulphate of alumina. The presence of the latter renders it very hygrometric and little fitted for its intended use. But there is a very simple method of remedying this drawback. If an equivalent quality of sulphate be added thereto it combines with the sulphate

of alumina to form an aluminate of ammonia. A product is thus obtained which remains as dry as ordinary phosphate. The chemical transformation then becomes :—

$$AlPO_4 + 3AmHSO_4 = AlAm(SO_4)^2 + AmHSO_4,AmH_2PO_4$$

If the Redonda phosphate contains, for example, 40 per cent P_2O_5, one calculates thus :—

100 phosphate	$40P_2O_5$
112 sulphate of ammonia	$24N$
130 sulphuric acid of 50° B.	$81H_2SO_4$
342	

We thus get a manure containing in round figures :—

	Per cent.
Nitrogen	8·0 [1]
P_2O_5 total	13·0
P_2O_5 soluble in water	11·0

In many cases it would be advisable to replace a portion of the nitrogen by potash. This substitution is easily effected. It suffices to replace the sulphate of ammonia to form alum by sulphate of potash :—

$$AlP_4O + 2AmHSO_4 + KHSO_4 = AlK(SO_4)^2 + AmHSO_4,AmH_2PO_4$$

The addition of potash in quantity greater than to combine with the alum complicates the work. It is clear, moreover, that one can likewise combine with this process the production of aluminate of ammonia ; the expense adherent to washing, evaporation, and crystallization appears, to be largely covered by the sale of the sulphate of alumina as a current article of commerce, whilst the richness of the manure would be increased at will.

By working as described, it is easy to utilize Redonda phosphate up to 90 per cent. As already mentioned, the sulpho-phosphate of potassium does not combine the conditions required in a concentrated potassic manure. Its sulphuric acid, amounting to almost 30 per cent, must be removed. Lime provides the easiest means. It has been proposed to combine monocalcic phosphate with sulphate of potash, but the process is not applicable because the gypsum is precipitated in the form of very attenuated crystals, which render filtration impossible after evaporation. But if lime in an insoluble form be used, i.e. as carbonate, and if it be made to

[1] If 342 of finished manure gives 24N, 100 only gives 7, not 8.—Tr.

react on the dissolved sulpho-phosphate of potash, the gypsum is precipitated in the same state, and its elimination from the liquid by filtration presents no difficulty. The free sulphuric acid of the sulpho-phosphate combines with the lime to form gypsum; by addition of phosphoric acid, the K_2SO_4 is again transformed into $KHSO_4 + KH_2PO_4$, and the acid of this new bisulphate is in its turn removed by $CaCO_3$. The sum of these reactions is represented by the following equation :—

$$K_2SO_4 + 2H_3PO_4 + CaCO_3 = 2KH_2PO_4 + CaSO_4 + CO_2 + H_2O$$

However, these reactions are not effected in such a simple manner. Thus the direct action of calcium carbonate on phosphoric acid is to form insoluble phosphate of lime. If it was desired to treat a mere solution of potassium sulphate in dilute phosphoric acid there would be a considerable loss of phosphoric acid. Moreover, the washing of the precipitated gypsum containing P_2O_5 and the evaporation of the wash water would entail great expense, capable perhaps of absorbing all the profit of the manufacture. An elegant and simple solution to the problem has been found by the use of grey phosphatic chalks. These phosphates, for which formerly no use could be found in spite of all the researches and tentatives made, contain about 30 per cent of $Ca_3(PO_4)_2$, and a preponderant quantity of $CaCO_3$; they are sold cheap. It is clear that, if in the process now described, calcium carbonate be added as phosphatic chalk, there will be obtained as a filtration residue a mixture of phosphate and gypsum, the phosphoric acid content of which is low but which can be perhaps utilized for the extraction of phosphoric acid. And if the phosphoric acid extracted from it is afterwards used in the manufacture of sulpho-phosphate of potash, it will suffice to treat the above phosphatic gypsum in the filter press to eliminate the adherent solution of potassic phosphate, but it would be useless to wash it, because the remainder of the potassic phosphate which it contains returns to the process by the extraction of the phosphoric acid. In this way the small amounts of phosphoric acid precipitated by the chalk would also be utilized. This detail also brings out better the advantages resulting from the use of phosphatic chalk in this case; in fact the amount of phosphoric acid precipitated is exceedingly small, because the conversion is effected in a less violent and more regular manner. Another very disagreeable drawback due to the carbonate of lime, is eliminated by phosphatic chalk; it is the entrainment of soluble potash by the gypsum sludge, owing, no doubt, to the formation of a double phosphate of calcium and potassium. The process just enunciated was the subject of a patent delivered to H. & E. Albrecht; it is applied on the large scale at the Biebrich factory, in the manner about to be described.

There is run into a lead-lined vessel, fitted with an agitator, a measured quantity of a 10 per cent solution of phosphoric acid, in which a corresponding quantity of sulphate of potash is dissolved. Afterwards, whilst constantly stirring the mixture, but without heating, the calculated quantity of pulverized phosphatic chalk is slowly incorporated. When, after about an hour, the conversion is accomplished, the phosphatic solution is separated from the residue by filter presses, and the liquor evaporated to a pasty consistency by steam heating. The dry salt is afterwards obtained, fit to be centrifuged by drying it in a special chamber heated by steam at a temperature of 70° to 80° C. From the filter presses, the residue falls directly into a second mixing tank with agitator, likewise lined with lead, and containing the quantity of sulphuric acid necessary to decompose the phosphate. When this decomposition is complete, the residue is separated from the liquid by means of the filter press, completing the extraction this time by washing, for the wash water afterwards serves to dilute the sulphuric acid. The filtrate, which consists of a mixture of phosphoric acid and potassic phosphate, flows from the filter press directly into the first receiver-mixer. The product thus obtained contains 38 to 40 per cent of P_2O_5 almost entirely soluble in water, 31 to 33 per cent K_2O, in addition to a few per cents of sulphuric acid, lime, etc.

The Salz Werke Co., Neustassfurt, have likewise succeeded in producing a pure and concentrated phosphate of potash from potassium chloride. The experiments made by this company led to quite an unexpected result. It is known that the metaphosphate obtained by the decomposition of potassic chloride, by phosphoric acid, at the temperature of fusion, is by itself completely insoluble in water, and even in acids. Now it has been found that by cooling it suddenly, it is converted into a modification very soluble in water. The decomposition is effected in a muffle furnace for sulphate, the evolved hydrochloric acid is condensed, and the liquid metaphosphate flows boiling from the oven direct on to cold plates, in a thin layer. After crushing, the product forms a dry salt easily preserved and containing 50 per cent P_2O_5 and 45 per cent K_2O. Although phosphate of potash, and similar concentrated manures, have not assumed, in agriculture, the importance that was at first anticipated, especially for cereal cultivation, they have none the less a great importance in certain special cultures, and above all in the Colonies, owing to freight charges, which are heavy. Their rational use in horticulture likewise presents very great advantages which will end by being appreciated. Here is an example: In the garden attached to the mansion house of Biebrich, in 1892, phosphate and nitrate of potash was applied to the raspberry plantations so as to obtain a heavier and an earlier yield. The success was such that the gardener of the mansion house had already sold £15 worth

of fruit collected in the squares so treated before the raspberries in the plants cultivated without manure were ripe (end of April). Now the amount used hardly came to the value of 1s.

Bisulphate Superphosphate.—It now remains to say a word about another product absolutely unpublished, i.e. the bisulphate superphosphate. Bisulphate, as is well known, is a bye-product of the manufacture of nitric acid, and finds hardly any use, except in glass works and in the manufacture of Glauber's salt. But it is difficult to sell, and it is got quit of at any price, for the local authorities forbid it being run into streams. Dr. Grueber tried to utilize it in the manufacture of superphosphates. By mixing 500 kg. of bisulphate with 150 kg. of Algerian phosphate he obtained a superphosphate, but the product was very deliquescent because it wanted the water of constitution necessary to the formation of sulphate of lime. Dr. Grueber remedied that by adding to the phosphate 60 kg. of water. He thus obtained a dry superphosphate, with 7 to 8 per cent of soluble phosphoric acid; the addition of a small amount of Algerian phosphate enabled it to be passed through the centifrugal crusher and to obtain it in a pulverulent form. As all manure factories require low superphosphates to adjust the analysis, this product would thus readily find a use.[1]

Phosphatic Peat.—It now remains to describe a manure in which the phosphoric acid is present, not in chemical combination but in simple admixture—we mean phosphatic peat. In 1892 the Society of German Agriculturists greatly recommended the manufacture of this product as a microbicide, as a preventative of epidemics, and fit to render both human and animal excreta inoffensive. The first steps made in this direction with hydrochloric and sulphuric acid have not given conclusive results; hydrochloric acid is too volatile, sulphuric acid carbonizes the fibre of the peat, so that it is difficult to use more than 2 per cent in the mixture. Phosphoric acid has not that drawback, and there is nothing therefore to prevent phosphatic peat being prepared with 10 to 15 per cent of P_2O_5. Experiments on a manufacturing scale, and application of this product, were made in 1893 by Dr. Meyer, who, moreover, exhibited samples at the show of the German Society of Agriculturists, who made him an award. There is no doubt that

[1] After the acid over and above that required to form the normal sulphate of soda was killed by the phosphate, the water very evidently acted by combining with the excess of sulphate of soda to form $Na_2SO_4,10H_2O$, an efflorescent salt. The "free" acid must have formed sulphate of lime *ab initio* or the phosphate could not have been dissolved. Of course the water would enable the dissolved phosphate of lime to react on the excess of sulphate of soda to produce phosphate of soda and sulphate of lime. But why not send the bisulphate up the cups and mix it in the mixer with the acid and phosphate in the usual way? This seems to have been a sort of compost heap, and the fewer of these about a factory the better.—Tr.

phosphatic peat possesses the properties which recommends it, more particularly for spreading on farmyard dung in stables. The excrements of animals commence to decompose as soon as they are eliminated by the animals, and this decomposition is accompanied by a great loss in nitrogen. The addition of the phosphoric acid not only retains all the nitrogen in the manure, but also enriches it. It also destroys the germs of infectious disease, typhus, cholera, etc., as the experiments of Fraenkel, Klipstein, and Burow have shown. Klipstein formally declares that phosphatic peat behaves better in this way than sulphated peat, which he had prepared with 10 per cent of sulphuric acid. The manufacture of phosphated peat is very simple. The peat is made to absorb the quantity of hot phosphoric acid diluted to the desired strength. Prepared peat or crude peat may be used. In the latter case, the peat should be passed through a slicing machine and then through a press. This manufacture should be profitable. To obtain the phosphoric acid the most impure phosphates, otherwise of no value, can be used; moreover, the phosphoric acid absorbed by the peat retains its solubility in water. On the other hand, it should not be very difficult to create a market, for peat has been employed for a long time as litter, as well as other additional matter, gypsum from superphosphates, which is spread in the stables. But there is no substance of this nature which possesses the antiseptic properties of phosphatic peat. It retains the nitrogen, destroys infectious germs, absorbs urine, purifies the air of stables, amplifies and enriches farmyard manure. The use of phosphatic peat for the disinfection of fæcal matter constitutes a problem more difficult to solve. The main obstacle is the system of everything to the drain, that all large towns have adopted to free themselves of their excreta in a radical but far from economical manner. In small localities (there are some in Germany where the use of phosphatic peat is obligatory) its purchase, its use, and the sale of the human manure under the control of the authorities, to prevent fraud, present real difficulties. But in large properties which have the use of the manure in their own hands, the use of phosphatic peat would be very rational in so far as one could then economize the cost of drying. But if it be desired to dry the manure, plant similar to that used to dry poudrette may be used. The manure, consisting of fæcal matter and phosphatic peat, after desiccation forms a manure analogous to guano. It does not give off any bad smell, and contains 4 per cent of N, 4·5 per cent P_2O_5 ($\frac{4}{5}$ soluble), 1 per cent potash and about 45 per cent of peat.

APPENDIX.

THE MANUFACTURE OF PHOSPHORUS IN THE ELECTRIC FURNACE.

In a recent publication of the United States Geological Survey, entitled "The Production of Phosphate Rock and Phosphorus in 1906," G. W. Stose makes an interesting summary of the progress made in phosphorus manufacture, and points out the rôle which the electric furnace has played in this development. Formerly phosphorus was only extracted from bones and other organic matter. It is only quite recently that it has been extracted from mineral products. First of all, phosphorus was extracted from phosphatic rocks, such as the impure fluophosphates of calcium, with which the superphosphates used in agriculture are generally made. Apatite, which is a fluophosphate or a chlorophosphate of calcium, was only used to a slight extent in Europe or in Canada. Quite recently wavellite phosphate of alumina has been used as a source of phosphorus. It is furnished in sufficient quantity for the purpose by deposits situated at Mount Holly Springs (Pennsylvania). The old process of phosphorus manufacture which was in use in the beginning of the nineteenth century is as follows. The bones are burnt, then ground; the bone ash superphosphate of lime is treated by a sufficient quantity of sulphuric acid to convert the whole or a part of the calcium into calcium sulphate and the phosphorus into metaphosphate of calcium and even into phosphoric acid, which is concentration by evaporation mixed with wood charcoal and reduced by heating in a furnace in a fireclay retort. The vapour of phosphorus and carbonic oxide is given off. The phosphorus which is condensed under water has a waxy appearance and yellowish colour. Theoretically the reaction should be :—

$$2Ca_3(PO_4)_2 + 6H_2SO_4 + 12C = 6CaSO_4 + 12CO + P_4 + 4H_2O$$

Practically, however, it is found that the following reaction better represents what occurs :—

$$3Ca_3(PO_4)^2 + 6H_2SO_4 + 10C = 6CaSO_4 + Ca_3(PO_4)_2 + 10CO + P_4 + 6H_2O$$

In this process the loss due to destruction of the retorts by sulphuric acid and by the great heat is considerable. Only a portion of the phosphorus therefore present in the charge is recovered. There is also the danger of seeing the phosphorus inflame when withdrawn, and it is necessary to take the greatest care to prevent the phos-

phorus condensing in the tubes and obstructing them. Numerous improvements or alterations on this process have been patented in recent years. Woehler was one of the first to heat phosphate of lime as it occurs in bone ash or phosphatic rocks with silicious sand and charcoal without resorting to the sulphuric acid treatment. Wing's patent, 1891, is based on the same principle.

Wing's Process.—In Wing's process, bone ash or pulverized rock phosphate and silica are moistened and made into balls which are placed by layers alternating with layers of coal in a *cubilot*. The coal yields the incandescent carbon required for the reduction of the phosphoric acid. The silica expels the phosphoric acid from the phosphate as anhydride P_2O_5, which is reduced to the condition of phosphorus by the incandescent carbon and the reducing atmosphere. The vapours pass to condensation chambers kept at a temperature of 500° F. (260° C.), in which the greater part of the phosphorus is deposited as red phosphorus and the remainder in a water chamber as white phosphorus. The process is continuous, the charge is introduced at the top through the furnace mouth, the residues are evacuated by the grate at the bottom, and two condensation chambers are used alternately.

In using the ordinary furnaces this method was found impracticable owing to the high temperature necessary to treat a charge as refractory as that just indicated. It is well known that electricity can furnish the high temperature necessary, and it was well imagined that it ought to solve the problem, but manufacture by this process has only become possible commercially quite recently, and since the invention of the electric furnace. Consequently the process has been introduced both in Europe and America, where it enables phosphorus to be made at a profit.

Readman's Patent.—This process, which dates from 1889, is applied in most countries. The bone ash or the crude phosphoric acid is mixed with ground coal or wood-charcoal. If mineral phosphate be used it is roasted, pulverized, and mixed with wood-charcoal, silica or a basic salt. The mixture is reduced in an electric furnace working continuously in a reducing atmosphere. The currents brought by retort carbon electrode traverse the charge placed between them, acts as a resistance and is heated to incandescence. The silica combines with the calcium to form a slag of silicate of lime. The phosphorus and carbonic oxide are given off as before. The disengagement commences at 1150° C. and requires a temperature of 1400° C., and even 1500° C. may be reached to complete the reactions. The reaction is the following :—

$$2Ca3(PO_4)^2 + 6SiO_2 = 6CaSiO_3 + 10CO + P_4$$

Harding's Process.—In Harding's process, 1898, the pulverized rock phosphate is heated with sulphuric acid ; the phosphoric acid

thus separated from the lime is filtered and evaporated to a syrupy consistency. It is mixed with granular retort charcoal, heated in a reverberatory furnace, and treated in an electric furnace, the arc issuing impetuously between the electrodes and traversing the mass. An atmosphere of hydrogen is produced by injecting petroleum spirit pulverized in the furnace.

Gibb's Furnace.—In this furnace, which was specially designed for the manufacture of phosphorus, the electric current instead of traversing the whole of the mass, passes without interruption into an intermediate circuit of great resistance, such as a cylinder of retort charcoal placed above the charge. This cylinder becomes incandescent and the arch of the furnace reflects the heat as in a reverberatory furnace.

Irvine's Furnace.—Readman's process was modified in Irvine's 1901 patent. The charge is made up as in the original method; however, phosphates of alumina or calcium may be used indifferently with the silica or basic flux. The two electrodes of retort charcoal are suspended vertically, and their lower parts reunited at the beginning of the operation by coal through which the current first passes. When the charge has melted, the slag formed collects on the top and reunites the two electrodes; that is, henceforth it is through this slag that the current passes. The fusion is continued, the excess of slag is run off as it is produced, so that the extremities of the electrodes are never uncovered.

Duncan's Patent. — In Duncan's process, patented in 1903, seventy-seven parts of ground phosphate are taken, whether of organic or mineral origin, twenty-three parts of ground coal, and mixed with tar acting as an agglutinant. The paste is dried, and after heating, which is done for economy in a hydrogen flame, a bye-product of the manufacture, the product is placed in an electrical furnace; this continuously produces phosphide of calcium. This phosphide in contact with water in an atmosphere of hydrogen, gives off phosphuretted hydrogens, which, when heated, are converted into red and white phosphorus according to the temperature at which condensation is effected.

Parker's Patent.—This process, which was patented in Great Britain by Parker in 1902, concerns the treatment of phosphate of aluminium. This phosphate is treated by sulphuric acid, then by a sulphate capable of forming an alum with the sulphate of aluminium, which is produced. All the alumina is separated by crystallization of the alum, and before the electric treatment. The residual liquid is mixed with coal or other bodies rich in carbon, and reduced in an electric furnace.

Landis' Method. — The American Phosphorus Company of Philadelphia possesses a factory at Yorkhaven where phosphorus is extracted from wavellite, using a method designed by G. C.

Landis, the company's chemist. The process, which is kept secret, is, as far as can be ascertained, analogous to that of Readman as regards the mineral and the furnace. The wavellite, the phosphate of aluminium, and the phosphate of calcium, are roasted, mixed with silica and wood charcoal, and reduced in an electric furnace which is one of the subjects of the invention. In January, 1907, a patent was taken out to protect certain improvements on the furnace, with the view of preventing the escape of gas or vapours or their absorption by the lining of the furnace. This is realized by the use of a second exterior lining made of non-absorbent bricks, and by the use of hydraulic joints for closing all the apertures of the furnace. The furnace is fitted with an interior lining of bricks of retort charcoal acting as electrode; there are also several vertical electrodes of the same material, which can be regulated either to establish a current through the charge or to form an electric arc. The slag is run off every three or four hours; the phosphorus vapours are condensed under water. It is very probable that it would be necessary to resort to a supplementary treatment to eliminate the alumina contained in the charge, and that the treatment is analogous to that used in the Parker process; that is the point which is kept secret. The phosphorus made by the greater number of the industrial processes is a crude white phosphorus having the appearance of yellow wax, and containing sand, charcoal, clay, and other impurities. These impurities are removed in different ways, either by filtering the fused phosphorus under water on wood charcoal or through a cloth, or by pressing by means of steam the fused mass through porous porcelain, or by redistilling it in iron retorts. The best method of purification, however, is again to treat the crude fused phosphorus, either by a mixture of bichromate of potash and sulphuric acid, or by hypobromite of sodium. Some of the impurities dissolve, the others collect on a scum which floats to the surface of the fused phosphorus.[1] Owing to its highly poisonous nature, and the danger in manipulating white phosphorus, attempts have been made to produce it in another form. Red phosphorus,

[1] There is no occasion whatever to dissolve these materials in the acid previous to mixing. If the acid be heated to about 150° F. and the shoddy, leather cuttings, greaves, scutch, etc., sent up the cups like the bone meal itself, the acid completely dissolves the whole in one operation. But that is in the case of mixings where there is no pretence of making dissolved bones, and an odd piece of core would tell no tale as it would in what purported to be a bone manure. The translator has sent as much as 4 cwts. of leather to the ton of finished mixing up the cups, and not a particle of it was to be seen in the aggregate 50 to 60 ton mixings when the doors of the "den" were opened three or four hours later.

As already mentioned, such materials as leather and shoddy are invariably used in Great Britain with mineral phosphates. They would absolutely spoil the colour of pure dissolved bones and at once point to sophistication.—Tr.

which is not poisonous, is easily prepared by heating to 250° C. the white variety in a closed vessel. It, however, has not the same properties as the crystalline white phosphorus. A crystalline variety of red phosphorus, recently discovered in Germany, is obtained by heating to boiling a 10 per cent solution of white phosphorus in phosphorous tribromide. This variety is not poisonous, and advantageously replaces white phosphorus in the manufacture of matches. The phosphorus industry is so new in France that it is very difficult to get statistical figures, moreover information is awanting on the state of the industry in other countries. The world's yearly production has been valued between 1000 and 3000 tons; up to quite a recent period this manufacture was localized abroad. The greater part of the world's phosphorus comes from the factory of Allbright and Wilson of Wednesfield, Oldbury, England; it was there that the Readman process was discovered. Its annual product may be 500 tons. There are other big factories at Lyons, France, at Griesheim and at Frankfort, Germany. There is likewise a factory in Sweden, and others, small and numerous, in Russia, of which six, situated near Perm, produced about 140 tons in 1890. In the United States, the first phosphorus factory was constructed forty years ago at Philadelphia by Moro Phillips; this establishment is still at work. The factory of J. J. Allen & Son was founded at Philadelphia in 1891, and in competition with imported phosphorus has furnished for a long time the phosphorus required by the Diamond Match Co., the largest match factory in the United States; but in 1897, the firm of Allbright and Wilson, under the trade name Oldbury Electro-Chemical Co., erected a factory of 300 H.P. working the Readman process at Niagara Falls, and it is this factory which up to now has supplied the Diamond Match Co., and furnished the greater part of the phosphorus produced in the United States. Recently that company has brought a new improvement to bear on the manufacture by installing Irvine's furnace, by means of which 80 to 90 per cent of the phosphorus contained in the raw material used can be extracted, which is a high strength rock phosphate. This result is comparable to that which the English factories obtain, extracting 86 per cent of phosphorus. There are six furnaces of 50 H.P., each with a production of 170 lb. of phosphorus per day, say an average of a total of 1000 lb. of phosphorus manufactured daily. The production varies according to the demand; however, the factory produces at the present time half of that which is produced in the United States.

The General Chemical Co. has recently acquired Duncan's patent, and another company is installed at Long Island, where they utilize for their furnaces the current which is distributed in the town.

The American Phosphorus Co. made its first installation at

Moore's Mill, near to Mount Holly Springs, Pennsylvania, where there is a mine of wavellite, which it possesses. The old method of heating by gas is used. The factory having been destroyed by a fire, another was constructed and started in March, 1905. Electric furnaces were installed and started during 1905, but the production of electricity by means of steam engines was too costly, and in 1906 the factory was transferred to Yorkhaven, Pennsylvania, where electricity yielded by a fall of water could be used. This company announces that it produces 500 lb. of phosphorus a day, and that it could produce 1200. The census of 1900 states three factories were at work in the United States, but that of 1904-1905 only shows the Oldbury Electro-Chemical Co. of Niagara Falls. Besides what it produces, the United States annually imports 30,000 to 40,000 lb. of phosphorus, which pays an import duty of 18 cents per lb. The price on New York market varies with the quality from 45 to 70 cents per lb.

CHAPTER X.

MANUFACTURE OF BONE DUST AND OF BONE SUPERPHOSPHATE (VITRIOLIZED BONES).

The use of bone dust as a manure goes back to somewhat distant times. It rapidly extended when Liebig advised that it should be dissolved by sulphuric acid, so as to obtain more rapid and certain effects. At the present time this product has to compete against nitrate of soda and basic slag. Moreover, certain manufacturers find it more advantageous to use bones in the manufacture of glue, and then to transform them into superphosphate afterwards. Whatever be the method of utilizing bones, it is indispensable previously to free them from fat, as will be seen in the sequel.

Chemical Composition of Bones.—The bones which form the framework of vertebræ, consist like all vegetable and animal matter of organic elements, and of mineral elements of combustible matter, and of ash. The combustible matter (moisture excluded) consists essentially of ossein (yielding gelatine) and of fat. Bone ash consists in great part of phosphate of lime. If the previously fat-extracted bones be digested with dilute hydrochloric acid, the phosphate of lime is dissolved, and a residue of ossein is obtained as a white elastic translucid substance which consists of:—

TABLE XLVIII.—CHEMICAL COMPOSITION OF OSSEIN.

	Per cent.
Carbon	50·1
Hydrogen	7·1
Nitrogen	18·8
Sulphur	0·2
Oxygen	24·2
	100·4

Ossein dissolves very slowly in boiling water when bones are boiled with water, and more rapidly when treated in a close vessel under pressure. By prolonging the operation for a sufficient length of time the bones can be completely freed from ossein. A residue of phosphate of lime is thus obtained with the initial form of the bone. Finally, ossein may be extracted by boiling with dilute potash lye.

On cooling, the solution of ossein previously concentrated by evaporation assumes a gelatinous consistency, and on drying it is converted into solid tablets which are marketed as glue. The ratio between the organic substance and the mineral matter in bones continually varies, not only with the origin and race of the animal from which they come, but also in one and the same individual, according to whether the bones are hard or spongy. In spongy bones the organic matter is higher by 4·5 per cent than in hard bones; the amount of carbonate of lime is likewise higher by 11 per cent, whilst the percentage of phosphate of lime is less by 15·5 per cent. It is evident that the percentage of nitrogen and phosphoric acid in bones is very variable. Their fat content calculated on the dry substance is from 10 to 12 per cent. Berzelius has given the following analysis of an ox bone freed from periosteum :—

TABLE XLIX.—ANALYSIS OF AN OX BONE. (BERZELIUS.)

	Per cent.
Cartilage completely soluble in water) Vessels „ „ „ „)	33·30
Tribasic phosphate of lime and a little CaF_2	58·35
Carbonate of lime	3·87
Phosphate of magnesia	2·05
Soda with very slight trace of NaCl	2·45
	100·00

This theoretical composition of bone built up from a select bone does not represent the average composition of the bones used by glue manufacturers, because the bones have undergone various treatments, such as boiling, fermentation, which may have altered their nature. Besides, bones are supplied by different animals. Practically ordinary bones received in factories respond in round figures to the following analysis :—[1]

TABLE XLIX. (A).—ROSINATE ANALYSIS OF BONES AS SUPPLIED TO MANURE FACTORIES.

	Per cent.
Moisture	12
Organic matter	28
Tribasic phosphate of lime and magnesia	44
Fat	10
Carbonate of lime, sand, etc.	5
	99

Commercial bones always contain more or less moisture, butchers' bones up to 30 per cent, and they are mixed with other

[1] This looks very much like an average analysis of ordinary "rag" bones. Ordinary London "rag" bones yield 11 per cent of fat when extracted by petroleum spirit.—Tr.

waste such as debris of skins, gut, etc. It is impossible to give a complete analysis, seeing the difficulty of taking a fair average sample. The skill and experience of the buyer, and inspection by a glance of his eye, are the best guides. Fossil bones naturally differ in their composition, thus their fluorine content rises to as much as 16 per cent. Müller found 17 per cent of gelatine in diluvian bones.

Fertilizing Value of Bones.—The use of bones as a manure has been known for a long time. They have been used for centuries in the manuring of vines in the south of France. Hunter, in England, drew the attention of farmers to bones in 1774. In that country the use of bones doubled and trebled the production of mediocre land, at a time when certain continental agronomists were still protesting against what they called the spoliation (*gaspillage*) by the bones used in fertilizing the land. England knew how to profit adroitly by this situation, by importing thousands of tons of bones at a vile price. At a certain time all the production of bones took the road to Great Britain, although it had itself an enormous production, and in spite of a rise in freights. In 1822, the battle-fields of Central Europe, in themselves alone, furnished her with 33,000 tons.

But the introduction of Persian guano, the pioneer of all other concentrated manures, completely altered the situation. There is not now to be found a single farmer who does give to bone manures all the credit which they deserve, even when he is indifferent to other manures. However, uncrushed raw bones are absolutely valueless to the farmer, as they do not become soluble in the soil until after a very long time. Now, in order to obtain good crops, the farmer requires rapid decomposition of the nitrogenous matter and of the phosphate in the soil. The bones must therefore undergo an appropriate operation. In chemical manure factories it is reduced to a fine powder or the gelatine is extracted from it, and it is afterwards made into superphosphate (dissolved bones). The use of bones in any other form is spoliation. Bone waste (fleshy fibre), which can be often bought cheap, should be similarly treated.

Storing, Classifying, Sorting and Crushing Bones.—Storing.—The first duty of the manufacturer is to bring all his care to bear on the storing of bones, because when they begin to rot they give off a smell which the workmen cannot stand. Besides, the decomposition of nitrogenous matter gives rise to a disengagement of ammonia, and there is a loss of nitrogen which may exceed 0·5 per cent. The drying of fresh bones requires fastidious and costly manipulations; that is why they rest content with sprinkling them with water containing 0·05 per cent of carbolic acid or with spirits of turpentine.

Classification of Bones.—Market bones are classified as follows:—

(1) *Kitchen Bones.*—These consist of ox, calf, sheep, goat, and some game bones. They are fresh, dry or fused (*fusé*, ? roasted). They often contain 20 to 25 per cent of water. Dry bones are called country bones. Their percentage of moisture is from 8 to 12 per cent. They are generally crushed and often fat-extracted by the vendors, which is readily recognized by the farinaceous tint of the bones on the outside. Fused bones enter into the class of the fossil bones; they are unfit for glue-making, for the organic matter has in great part disappeared owing to fermentation and exposure to all sorts of weather. Amongst kitchen bones are to be found sheep bones and those of kids, with down, and pork bones, which are less esteemed. Kitchen bones generally contain remains of horns, horn-piths, glass, scrap iron, earth, bread. Hand picking enables the value of the goods to be appreciated.

(2) *Horse Bones or Knackers' Bones.*—These bones yield a less valuable glue than kitchen bones, and they have to be sold cheaper. Ten per cent of these bones are tolerated amongst kitchen bones. The fat and glue which they yield are inferior.

(3) *Buried Bones.*—Buried bones are those of animals (ox, horse) which have remained a certain time in the ground to destroy the flesh. They are the bones of infected animals which have taken a bistre colour owing to burial. They are depreciated and the manufacturer refuses those with hanging flesh.[1]

(4) *Bullocks' Heads and Canards* (*Sheep's Heads*) pass into the kitchen bone class, but they are generally sold apart for the acidulator (? glue maker,? manure maker: both are acidulators).

(5) *Scraps and Waste.*—These are the residues of the "turnery" trade. They are in great request for acidulation and are sold separately.

(6) *Hornpiths.*—They are used like "scraps" for acidulation. They are fresh or dry. The dry piths are often fused and are then of less value.

Bones, therefore, in consequence of the different material which they contain, are classed and assorted so that the operations which they have to undergo furnish satisfactory products. As the bones are most often mixed with impurities which are of a nature to damage the machines, it is necessary to pick or assort them.

Bone Picking.—In factories of a certain size the picking is done on shaking tables, driven mechanically or by means of large sifting machines, both appliances being fitted with meshes of $\frac{2}{3}$ of an inch. Soil and small particles of bone fall through the grating, whilst

[1] The resurrection of the bones of infected animals is a most dangerous practice. The earth mould from the remains of animals dead of anthrax is still infectious after twenty years.—Tr.

horns, glass and scrap iron are separated by hand on the shaking table, or on a revolving table placed at the end of the shaking table, or the sifting machine. Generally, they rest content with receiving the bones on an inclined endless band, along which the female sorters are arranged. The band moves slowly, so as to give time for sorting, and its slope enables the bones to be fed into the hopper of a bone crusher. Before falling into the crusher, the bones issuing from the chain fall on to a narrow iron plane inclined at 45°, divided into two parts and soldered by a copper band. Each of these parts corresponds to one of the poles of a strong electro-magnet situated underneath. It follows that if the iron falls on the inclined plane it is retained, and eliminated by the sorter who had allowed it to pass on to the chain. In this method of sorting, the earth necessarily follows the bones into the crusher; nevertheless, a certain part of the earth is not fed on to the chain when the man feeding uses as a shovel a fork with close teeth in shovelling the bones thrown on to a perforated sheet of iron over a pit where the earth collects. Although this earth may be removed in subsequent operations, it is always more advantageous to remove it before crushing, so as not to have pulverulent matter in the fat extraction and in the glue autoclaves. There is little useful matter in this earth, from which the small particles of bones are removed by finer sifting. They are mixed with bone meal for manure.

Bone Crushing.—Two sorts of tools are used in bone crushing; one working at a slow speed, which is the toothed crusher, and the centrifugal crusher at great speed, such as that constructed by Weidknecht. It is well to have several successive crushers with duplicate exchange pieces, so that they may be replaced rapidly. The first crusher is the coarse crusher, and the second the finishing mill.

(1) *Slow-speed Crusher.*—It consists of two large rolls formed by thick circular toothed bosses and with teeth a little obtuse, alternately with non-toothed bosses of the same thickness, but of a less diameter by the height of two teeth; the aggregate of the bosses is mounted on a hexagonal steel axis. The rolls are fitted up in such a manner that the teeth of the one correspond to the circular part of the smaller diameter of the other. They are separated by the space desired, to crush coarser or finer. For that purpose, they are driven by steel cog-wheels with deep teeth, allowing a certain displacement. One of the rolls is on movable bearings, capable of sliding if the resistance to be overcome is too great, being brought back to the original position by a system of springs. A good fly-wheel is necessary to overcome passing obstructions. The crushers built by Krupp attain the same end, and are made of very hard special steel. There are two crushers, the one after the other, fed by cup chain elevators in the case of the second crusher, so as to

arrange two pair of rolls on the same framework. The second crusher has shorter teeth, and its rolls nearer. The largest pieces issuing from the second roll must not be larger than a small hen's egg, in order subsequently to get a good fat extraction.

(2) *Very Quick-speed Machine.*—To this class belong Weidknecht's (F.) and Carr's. Weidknecht's excellent crusher consists of a very strong framework properly so-called of cast-iron in two pieces, the lower part or pedestal, and the upper part or hood; these pieces are bolted at their point of contact. The hood is adjusted to the framework, on the one hand, by a joint forming a hinge, and on the other hand by a screw and bolt joint. By this arrangement a single workman is able to inspect the machine, or change the grating in a few minutes. All he has to do is, by a turn of the spanner, to reverse the screw of the bolt joint, and to lift the hood which hinges on its axis. The bearings are of great scope and constant lubrication. Moreover, to diminish the friction surface of the shaft, the plummer blocks are suppressed, and to keep up the lateral play they are replaced by abutment screws which are fitted to each end of the shaft and in contact with the tempered sheaths adjusted consequently in the end of the shaft.

The shaft thus maintained is filled in its middle with a jacket or boss, on which fixed levers are arranged, at the end of which levers hinged hammers are fixed which work like flails, the hinge enabling the hammer to fold itself back when at work if overfed or if a foreign body be fed into the machine. The mobility is also intended to keep the machine from stopping if the belt comes off, if it be not fed automatically. In fact, the hammers, by folding backwards, let the fine material pass through the grating arranged in the lower part of the framework; the apparatus being thus freed, the shaft regains its normal speed without having to stop. The hammers thus form a fly-wheel, storing up active energy. The machine is fitted on its interior lateral faces by toothed steel plates of great hardness; they are kept in position by bolts and can thus be easily replaced. The hood or upper part is fitted up in the same way on its lateral faces; moreover, it has on the roof linings, likewise fitted with projections, and fixed by bolts on the shaft is the driving pulley. The machine is in fact very strong, and the pieces easy to replace. There is no heating in spite of the speed, for the ventilation due to the motion is very energetic. The fineness of the product depends solely on the dimensions of the grating, which in the case of bones consists of bars wide apart, through which the hammers drive the crushed bones. A crusher with bars less far apart acts as a final crusher, and, as before, a chain cup elevator serves to feed the second with the crushed bones from the first.[1]

[1] But each machine built on the disintegrator principle is sold to make fine bone meal. Although the translator has not had much experience of bone crush-

It is asserted that crushers working by shock develop more heat than need be. With crushers such as those described working at a great speed, with the bars of the grating far apart, the temperature does not rise more than with a toothed cylinder, for the ventilation is very energetic and the friction reduced by the width of the passages.[1]

Extraction of Fat from Bones.—The extraction of fat from bones is an indispensable operation, even when it is a question of merely converting the bones into dust for the farmer. In fact, bone dust not deprived of its fat is of less value, because the fat decomposes very slowly in the soil, and constitutes an obstacle to the phosphoric acid becoming soluble.

Fat may be extracted from bones by three processes: (1) By simple boiling in open pans. (2) By the action of steam in closed vessels. (3) By solvents. The extraction of fat by simply boiling leaves the ossein almost intact, but generally there is only obtained a portion of the fat in the bones.

By extracting the fat by steam, a higher yield of fat is obtained, especially if the operation be continued long enough, but a portion of the ossein is then transformed into gelatine. Now, in manure manufactories this gelatine constitutes a loss and becomes cumbersome because it decomposes rapidly; if it be diverted into a stream, it infects the rivulets. It is best used in irrigation. Bone dust from bones treated by steam is more soluble than that of bones from which the fat has been extracted by simple boiling; moreover, it is also more in request by farmers.[2]

ing by two machines running tandem as it were, yet here the fine meal made at the outset apparently passes along with the core to the second machine, which it would most certainly block up if fed into it as rapidly as it came from machine No. 1. The crushed bones from No. 1 machine should certainly be screened before passing to No. 2, so that the hammers can get at the lumps without the smaller particles removed by the screen acting as buffers. There is no getting over the fact that the grinding of bone meal by such machines is costly. It is a pleasant sight to see one go ahead for an hour. It is another to see four or five men idle through blocking up for a quarter to half an hour.—Tr.

[1] The bearings should be kept clean and free from dust as far as practicable; oily bone dust is liable to set the bearings aflame. The bearings should be covered during grinding and only uncovered for lubrication. Machines revolving at 2000 to 3000 revolutions a minute develop quite enough heat on the bearings without it being increased by fine air-driven bone dust.—Tr.

[2] As far as Great Britain is concerned the translator dissents (see previous note). Moreover, there is no absolute necessity whatever for the manure manufacturer to turn bone boiler, whatever there may be for the bone boiler to turn manure manufacturer.

Whether fat extracted or non-fat extracted ground bones decomposes most rapidly in the soil, will depend on circumstances. Many years ago the translator superintended the dispatch of some 30 tons of bone meal made from rag bones, i.e. non-fat extracted. The next year the same customer was supplied with ground bones from bones that had been boiled under pressure. He made a most

But this preference is not justified, for bone dust from steam-extracted bones is less rich in nitrogen. The extraction of bones by solvents (benzene, petroleum, ether) gives a larger yield in tallow whilst preserving integrally the ossein of the bones; these then form a powder rich in nitrogen. This process is undoubtedly to be preferred whatever may be the point of view at which it is looked (manufacture of gelatine, or manufacture of manure). It is the only rational process to apply.

Extraction of Fat from Bones by Water.—This process is the most ancient, and recalls the skimming of the cook's "stock" pot. In a cylindrical cast-iron pan a little wider below than above, there is introduced by means of a crane a basket of perforated wrought-iron containing about one-half ton of bones. The bottom of this basket, likewise perforated, can open into two semi-circular parts held by hinges on a cross bar, dividing the basket into two equal parts. These two doors are closed by hooks, so as to receive the charge. The basket is cylindrical, a little smaller in diameter than the pan which contains it, and shorter by 4 inches. A strong circular hoop at the top supports the sheet iron, and carries four strong handles, by means of which the cross-piece of the crane can lift it. The cast-iron pan is fitted with a gutter or throat, so as to separate the fat from the water in a continuous manner. The basket, therefore, being charged with bones in the fat extraction pan, water is run in to immerse the bones and steam caused to bubble in the bottom from a perforated steam coil. The water, brought to about 100° C. (212° F.), causes the fat to rise from the bones through holes in the gutter at the same time as the excess of water. The fat flows constantly from the gutter by the horizontal exit tube, whilst the water in the bottom issues through a bent tube without taking any fat with it. The exit of the fat may be facilitated by a superficial push, or by a paddle driven mechanically, mounted on a vertical shaft fixed on the side of the pan, capable of being rotated and raised at the end of the operation, so as to allow the basket to be freely removed from the pan. The bones are extracted in this way for about an hour and a half, after which they are removed from the basket to the washer. Certain factories slightly acidulate the water by an addition of sulphuric acid, 4 litres for 500 kg. of bones (say 1 gallon for ½ ton), so as to free the grease from its calcareous compounds. There is obtained 1 to 5 per cent of fat according to the quality of the bones. The same water can

grievous complaint, and he was right too, because boiling removes ammonia. Bones, the fat of which is extracted by petroleum spirit, are possibly not depreciated in value to the farmer. The author seems to have written this chapter more from the point of view of the glue manufacturer than the maker of artificial manures. The farmer who knows his business will not take ground steamed bones when he wants ground kitchen or rag bones.—Tr.

serve for several successive operations, and finally gives a boiling of gelatine concentrated enough for making glue. If gelatine be not made, the boilings are collected and concentrated by evaporation to add them to the bone dust as shown in the sequel. But the same water cannot serve indefinitely for fat extraction. After a certain time, it is remarked that the fat which it dissolves no longer rises to the surface. The solution takes a milky appearance; it is a sign that it is saturated with gelatine and that its concentration obstructs the ascent of the globules of fat. It must then be drawn off and replaced by fresh water. Unless fresh bones are operated on, the fat obtained on extraction by water is generally of inferior quality, it gives off a bad smell and is more or less dark in colour. It is purified as indicated further on.

Fat Extraction from Bones by Steam.—Fat extraction from bones by steam is done in large cast-iron cylinders, capable of containing 4 to 5 tons of crushed bones, the upper opening serving for the introduction of the bones, the lower opening for their discharge. These openings are closed by hinged lids as in an autoclave. Steam enters at the top and the fat runs off from the bottom by means of pipes situated near the aperture. Steam of from two to four atmospheres is used; for one to two hours the steam entrains the fat with it. The condensed water, charged with fat and gelatine, collects in the space reserved below the false bottom and is afterwards added in the manufacture of nitrogenized superphosphates, although the fat exercises an unfavourable influence on the dissolving of the phosphate. This water generally contains 1 to 2 per cent of nitrogen and 0·3 per cent of P_2O_5, in the concentrated state. It contains as much as 7 per cent of nitrogen, 3 per cent of ash, 50 per cent of organic matter, and 45 per cent of water. The solution of fat and gelatine is withdrawn from time to time, and the treatment by steam continued until a sample of the liquid contains no more fat. To separate the two, the different draw-offs are united in a wrought-iron pan with a conical bottom, fitted with a steam jacket into which steam is injected, and a tap for drawing off the fat. The object of heating is to keep the gelatine fluid enough for the fat to separate on standing. When separation is complete, the fat runs off by the above-mentioned tap, and the gelatine is run into an evaporation pan through a valve in the conical bottom of the pan. Whatever may be the quality of this gelatine, it may be of advantage to reduce it to a marketable form by a series of manipulations which the author has described elsewhere. By submitting bones to systematic storing, all the gelatine may be extracted, and the resulting bone dust, almost destitute of nitrogen, contains 35 per cent of phosphoric acid. Bone dust is often mixed with moist superphosphate to dry it.

Some manufacturers only make degelatinized bone dust which

constitutes an excellent food for animals and a very active chemical manure for meadows.

The fat extracted from bones by steam has perceptibly the same colour as that got by boiling, but it is of better quality and gives off a less unpleasant smell. When the bones treated have begun to decompose, as very frequently is the case, the volatile bad smelling products are in great part volatilized during the operation. Bang and Ruffin have suggested steaming combined with centrifuging. The fat with a little gelatine can first be extracted in a centrifugal machine, then the gelatine. This process has not been adopted by bone-boilers, but it is used in extracting fat from fish.

Extraction of Fat from Bones by Benzine.—For a long time efforts were made in France to extract fat from bones by benzine. Deiss used carbon disulphide, but as the bones, the fat of which was extracted by this solvent, gave bad quality glues, the process hardly extended. In 1871, Vohl suggested canadol (gasolene) as an advantageous substitute for carbon disulphide; then in 1876 M. Terne took out a patent for extraction by petroleum benzine, in America, whence this industry spread to Europe. Petroleum benzine presents, in fact, less danger than carbon disulphide, and its condensation is more easy because it boils at a higher temperature. The apparatus constructed by Mr. Deroy, sen., for extracting fat from bones by petroleum benzine consists essentially (Fig. 36) (1) of an extractor A with a perforated false bottom, and steam coil; (2) of a recuperator B or distilling pan; (3) of a condenser C; (4) of a pump E for circulating the solvent. *Working.*—The routine of the operation may be resumed thus. A certain amount of water is run into the extractor according to the capacity of the apparatus, so as to preserve the coil and the taps from the attack of fatty acids. Afterwards, the extractor is charged with crushed bones free from foreign matter. As soon as the charge amounts to a quarter of the capacity of the apparatus, the pump is started, and a beginning made by drenching with benzine the bones introduced. During this time the autoclave is charged in such a way that the solvent constantly bathes the bones, which enables the interposed air to escape freely. When the apparatus is full the top stopper of the extractor is closed and the tap 23 on the condenser opened. The air is allowed to escape until condensed benzine appears; the tap is then turned and the pressure allowed to rise to $1\frac{1}{2}$ kgs. on the manometre (9). This pressure once reached, the steam tap is closed and the apparatus allowed to rest till morning. The benzine is charged with all the fat of the bones, and the vapours are totally condensed. The next morning the apparatus is emptied into the distilling pan, and after a rest—about ten minutes—the water, previously run into the autoclave, and which now occupies the bottom of the pan, is withdrawn. The benzine is then recovered by distillation and by pass-

ing it through the condenser C, by means of the gooseneck 13, and the tap 24; it goes to the reservoir E. The benzine impregnating the bones is subjected to a current of steam, which finishes by entraining it into the distilling apparatus. When it has been made certain that nothing but water passes in the distillate, the extractor is emptied, first opening the lid of the top manhole, and then the

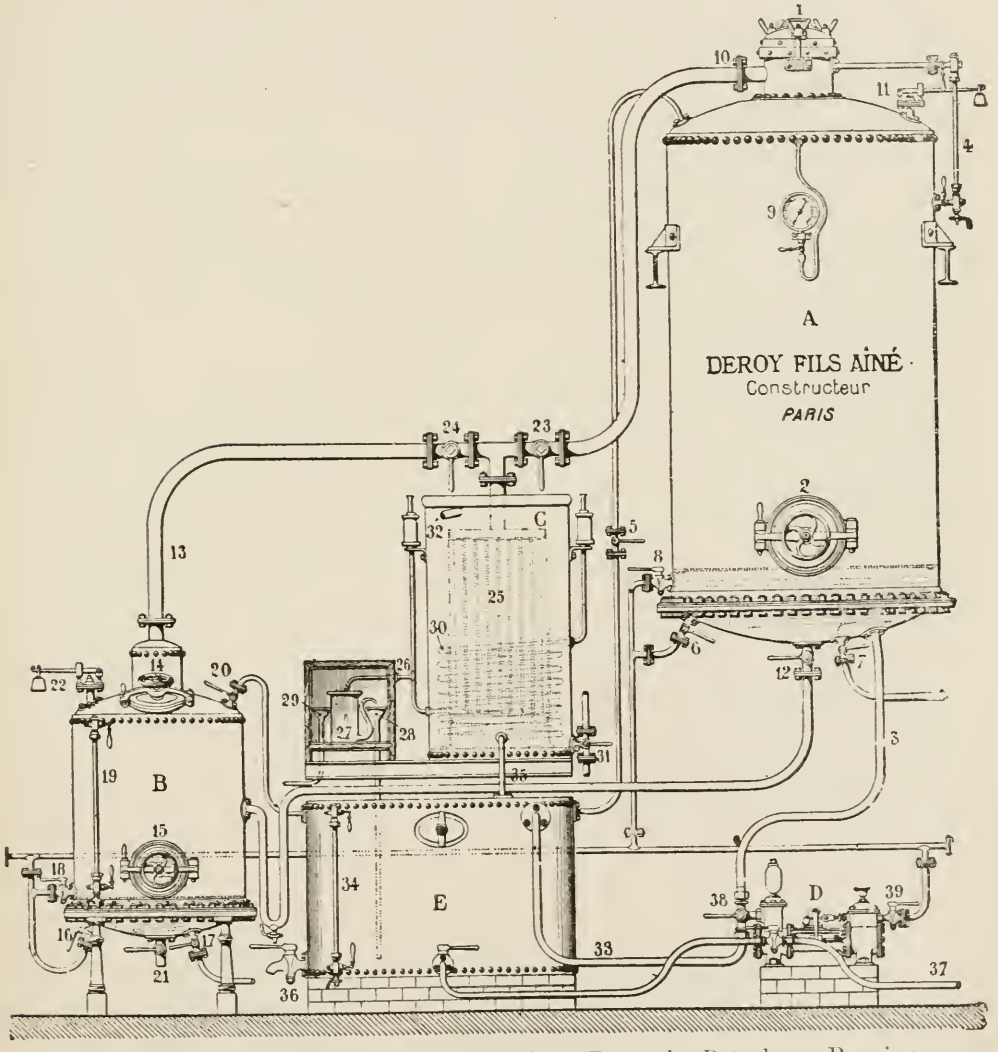


FIG. 36.—Plant for Extraction of Fat from Bones by Petroleum Benzine.

bottom one. The distillation is urged until no more petroleum benzine distils. At this moment a current of steam is injected into the fat by means of a perforated steam coil which carries off the last traces of solvent. The fat can then be drawn off from the distilling pan by the tap 21.

Purification of Bone Fat.—Fresh bone fat is naturally whiter

than the fat from ordinary country bones (? rag bones). It is purified by treatment in a lead-lined pan, by water acidulated with sulphuric acid, of which an excess must not be used. The fat and the acidulated water are then heated by a perforated steam coil, which beats the two up together. After some time the tallow shows clear and no turbidity in the spoon. The steam is turned off and the whole allowed to stand. The mixture of tallow, gelatine, carbon and phosphate of lime, and fatty acids combined with lime is destroyed, the gelatine is dissolved and oxidized by the acids, and the lime is precipitated as sulphate of lime with various impurities. After sufficient resting, the layer of fat is separated by means of a pipe hinged to the draw-off tap.[1] This pipe enables the pure fatty layer to be run off and to reject the water and sulphate of lime. The purified grease falls into a wooden vat lined with lead, where it is washed several times with boiling or simply tepid water. After which it is let stand and drawn off as before into casks for use in soap works or candle works.

Bone fat is often bleached as follows :—[2]

To the melted fat mixed with half its volume of water, 2·5 per cent of chlorate of potash is added and enough hydrochloric acid to decompose the whole of the chlorate. An excess of this acid is added to neutralize calcareous compounds. The tallow is purified and whitened with 2·5 per cent of chlorate and a semi-tint obtained ; with 5 per cent of chlorate a whiteness of the tallow is obtained analogous to that of lard. It is washed several times with water, until the wash water is free from chlorine, which is recognized by iodized paper. Bleaching by sunlight is equally energetic. The fat must be run into shallow vats which are exposed to the light. Agitation in presence of ozonized air also constitutes a method of bleaching. At the normal temperature, bone tallow is soft, unctuous, and does not rancidify easily. Although insoluble in water, like all fats it contains about 2 per cent of water, which it is impossible to eliminate even by heating it to 100° C. To obtain it in

[1] Bone fat is rather too viscous and easily cooled to be readily syphoned. It is transferred from the refining pan to the wash pan by short-handled ladles or dippers, and filled from the wash tank into barrels standing alongside by the same dippers. After the bone fat has cooled and set the casks are headed up by a cooper or handy man.—Tr.

[2] The author does not differentiate between the bleaching of white bone fat got by boiling of fresh bones and of brown bone fat got by extracting rag bones by benzine. The best results the translator got with chlorine as a bleaching agent of brown bone fat, was a canary colour. Brown bone fat takes up tons of water to form a white *emulsion*, but deprived of the emulsive water, it is a long way off white. Sulphurous acid is said to give good results, and possibly in soap-making it could very well be bleached by hydrosulphite or "blankit" in the soap-pan. But possibly it is impossible to eliminate the fusty smell of brown bone fat even from soap made from it.—Tr.

an anhydrous state, it is necessary after having refined it to heat it up to 150° C., and to maintain it for some time at that temperature. But it easily finds a buyer even when it contains a little water.

Manufacture of Bone Dust.—Fat extracted non-degelatinized bones are reduced to powder which passes through a No. 50 sieve and dispatched to farmers without other treatment. If on the contrary the bones have been deprived of the greater part of their nitrogen, they decompose with difficulty in the soil, and it is better to convert them into superphosphates. The crushers used being the same in both cases, the reader is referred to the description already given. The mode of action in the soil of the non-degelatinized bone dust is based in the first instance in the solubility of phosphate of lime in putrefying gelatine. It behaves in a certain sense like raw Peruvian guano, which has been described, and in which the basic phosphate of lime is rendered soluble by the nitrogenous elements which accompany it. The bone dust in the soil is distinguished by this peculiarity, that its phosphoric acid is not absorbed by the soil, and it can thus penetrate into the deeper layers, whilst every other solution of phosphoric acid is retained by the surface soil. This property of bone dust is sometimes of great benefit to the farmer. The return in the same soil during several successive years of plants with a tap root, may have exhausted the subsoil of phosphoric acid. In that case bone dust furnishes the means of restoring to it new stocks of that element so necessary to vegetation. The finer the bone dust the more easy is it dissolved and decomposed. Coarse powder only acts feebly, but its action makes itself felt for several years. The fine powder decomposes rapidly in the soil and acts energetically the first year. That is why farmers always require a fine powder. It is to the interest of the manufacturer to please them by looking after the crushing and the grinding of the powder. Bone dust made from fat extracted bones has the following composition, according to Holdefleiss :—

TABLE L.—ANALYSIS OF BONE DUST FROM FAT EXTRACTED BONES.

	Per cent.	
Nitrogen . . .	4·14	
Phosphoric acid . .	21·68	say 45 per cent $Ca_3P_2O_8$
Water	6·51	and 1·49 per cent $Mg_3P_2O_8$
Organic matter . .	36·29	
Carbonic acid . .	2·30	
Sulphuric acid . .	0·41	
Lime	27·83	
Magnesia . . .	0·68	
Oxide of iron . .	0·37	
Fluorine . . .	0·52	
Sand	3·60	

Stored and fat extracted bone dust does not contain more than 2 to 3 per cent of fat.

The efficiency of bone dust as manure has been the subject of many discussions. P. Wagner and Mercker seem to have misunderstood its fertilizing value, whilst other experimentalists have obtained excellent results. According to recent experiments, it is recognized that the efficacy of bone dust was perceptibly increased by an addition of solvents (? conversion into vitriolized bones); nitrification bacteria likewise intervene. A small quantity of the solvent (sulphuric acid) suffices to give to bone dust a remarkable activity, as experiments on this point testify. This agent has the effect of disintegrating the bone dust, and rendering it soluble in citrate. Stoved bones, non-fat extracted nor degelatinized, do not dissolve in a satisfactory manner. The organic matter of such bone dusts is transformed into a gluey matter very difficult to dry.

Classification of Bone Dust.—J. Konig has proposed the following classification of bone dusts:—

1. *Normal Bone Dusts, or Bone Dust No.* O.—Those bone dusts which are made from bones which have not undergone any treatment for the extraction of gelatine, and containing 4 to 5·3 per cent of nitrogen and 19 to 22 per cent of phosphoric acid, in which, moreover, after deduction of the matter extractable by chloroform is as 1 : 4 to 5·5.

2. *Bone Dusts* (*without any other designation*).—Those bone dusts which contain 3 to 4 per cent nitrogen and 21 to 25 per cent of phosphoric acid, and in which after deduction of the matter extractable by chloroform, the ratio of the nitrogen to the phosphoric acid is 1 : 5·5 to 8·5.

3. *Degelatinized Bone Dusts.*—Those which contain 1 to 3 per cent of nitrogen and 24 to 30 per cent of phosphoric acid, and in which after deduction of the matter extractable by chloroform, the ratio of the nitrogen to the phosphoric acid is 1 : 8·5 to 30.

To these kinds of bone dusts must be added the bone dust made in some countries from raw bones. However, there is sometimes sold as raw bone dust the waste from bone-black making after the extraction of the fat by benzine. Nothing should be designated as raw bone dust unless actually made from raw bones. [The bone-black factories sieve the bone dust from the meal or granules before charring the bones, as the dust is not so efficacious as a decolorizer as the granules.—Tr.]

4. *Mixed Manure Dusts.*—The manure dusts which after deduction of the matter extractable by chloroform containing 1 per cent of nitrogen as ossein, and in which the ratio of nitrogen to phosphoric acid is from 1 : 30, should not be designated as *bone dusts*, but as *mixed manure dusts*.

Meat Dust (*Meat Meal*).—An exception to this rule is formed by the manure prepared in the manufacture of meat extract, and which ought to be designated as meat dust (meat meal), which suffi-

ciently differentiates it from the above-named bone dusts. Thus established, the differentiation of the different qualities of bone dusts is very sharp, and they are no longer confused with mixture of horn, hair, etc.

Adulteration.—Bone dust is the subject of numerous sophistications. Finely crushed gypsum and corozo powder are often found therein, substances which it is impossible to recognize by the naked eye. In that case the analysis of the product shows that its percentage of nitrogen and phosphoric acid is inferior to the normal, for corozo only contains 2·44 per cent phosphoric acid and 0·96 per cent nitrogen, and gypsum contains neither of these ingredients. But the most frequent adulteration consists in adding to it phosphorite, or the phosphatic lime of the glue manufacturers, or a mixture of phosphate of lime and greaves. As all these products are rich in phosphoric acid, their effect is to increase the total phosphoric acid of the product, and to diminish considerably its percentage of nitrogen. To hide as much as possible the difference between the two elements which would be revealed by analysis, sophisticators resort to sulphate of ammonia. But, as already pointed out, the essential element besides phosphoric acid is ossein, or gelatine, which cannot be replaced by nitrogenous debris of animal origin, and far less by sulphate of ammonia. The above sophistications are therefore very prejudicial to the farmer, even if he receives in that way more nitrogen and phosphoric acid than furnished to him by normal bone dust. The mixture of phosphorite or of phosphate of lime and ammoniacal salt can never replace bone dust. No more can the mixture of phosphate of lime and greaves replace it, for the nitrogenous elements of this mixture do not consist of ossein, but rather of a substance analogous to horn.

As regards the impurities, sand, etc., and the degree of moisture, they should not exceed certain limits. Like all pulverulent substances, bone dust draws moisture from the air and the manufacturer cannot be responsible for it. The normal moisture is 4·7 and the percentage of sand 2·4 per cent.

Manufacturing of Bone Superphosphates.—As just seen, bone dust differs in composition with the nature and quality of the bones from which it is derived and the method of manufacture. In normal bone dust, the ratio of the nitrogen to the phosphoric acid is as 1 : 5. Generally, however, there is found 0·5 to 1·0 per cent of nitrogen from different debris of animal origin. Bone dust of this nature may be delivered to farmers without other treatment. But if the ratio between the nitrogen and the phosphoric acid is less, say 1 to 6, or beyond (Holdefleiss found a sample was 1 : 23·55), it is a proof that the bones were too much degelatinized, and the dust is of less value if used directly as manure. It would behave in the soil like a mixture of normal bone dust and phosphorite powder,

or if its percentage of nitrogen has been artificially increased, as a mixture of normal bone dust, phosphorite and of dried blood. All the phosphoric acid in excess above the ratio of the proportion of ossein nitrogen to phosphoric acid should be regarded as raw phosphate, and of no value to the farmer.

But these sorts of bone dusts yield excellent results if converted into superphosphates. In fact, if all the phosphoric acid be dissolved, the latter has no need of ossein in the soil; the bone dust so treated constitutes a nitrogenized superphosphate. The manufacture of bone superphosphate (pure dissolved bones) is very simple.[1] The bones, previously crushed and degreased, are reduced to powder

[1] The author does not quite do justice to the grave technical difficulties which beset the making of pure dissolved bones. It is almost an impossible task. The difficulties begin at the outset. First of all, working with a mixer that will easily make 2½ tons of mineral superphosphate at a mixing, the charge must be reduced to ton mixings, and with certain intractable bone meals to ½ ton mixings. The reason is that the interaction between the acid and the bone dust is more energetic than in the case of mineral phosphate, and owing to the rapid formation of sulphate of lime the mixer tends to set. This perforce leads to the use of water to get the charge out of the mixer. In the "den" the finished mass looks like dirty porridge, white inside but brown on the surface where exposed to the air. The only way to dry it is to cut it into pieces with the shovel and sprinkle it with bone meal, dry in an oven, and then try to coax it through a wide-meshed screen with more bone meal and then through a finer screen again with more bone meal. Bone superphosphate, pure dissolved bones, vitriolized bones, will never dry in the heap. But the translator found it to dry well in the sun by turning the pieces over and sprinkling with bone meal. It will thus be seen that to make pure vitriolized bones is a costly operation and one which in no way pays the conscientious manufacturer who looks askance at any order for it. As to putting bone black up the cups before the bone dust, the only advantage the translator can see is that the bone black is more tractable, but he never found it to have any great drying properties. Bone ash if available would be far less objectionable. For one thing it would not make the manure unsaleable. Farmers when they see a black manure always think of soot, and the translator will always remember the anathemas hurled at him by a farmer whose order for a 37 per cent soluble phosphate he had executed with a bone black superphosphate. A little bone black goes a long way, as paint manufacturers know, and a farmer decidedly objects to a manure as black as his hat. He can only test the manure organoleptically, and he flatters himself he knows soot when he sees it. But then a pure dissolved bone should consist of nothing but raw bone and acid. Strictly speaking, bones treated for their fat or their gelatine cease to be bones, and their definition must be qualified. As to the addition of nitrate of soda in the mixing, that will give a good deal more than 2 per cent of salt cake in the dissolved bones, and that can only be looked upon as an adulterant. Besides, nearly ½ cwt. of nitre to the ton of bones would mean that the operation, owing to the fumes, would be insupportable, as the steam rolls off in billows and it only wants nitrous fumes to make the position of the man at the mixer a far from enviable one, especially with a mixer that is open or half open during the mixing process. Again, why should the manure manufacturer lose 5s. per ton of bones for which he gets no credit? All the same, nitrate of soda up the cups will no doubt help the dissolved bone to dry, and as a matter of fact it assists all manures, but a black draught may gas the man at the cups who cannot well get away from it. A rapid current of warm air is what is required to dry vitriolized bones. Drying machines like Figs. 32 and 33 should be effectual. Stewing in an oven with a poor draught is not at all effectual and chars the manure.—Tr.

by means of a steel ball mill, or by a Carr's disintegrator. The powder yielded by the crusher is then passed through a No. 50 sieve, and the core returned to the crusher, which finally reduces it to the desired fineness.

The bone dust is then mixed with the desired amount of dilute sulphuric acid, using the same mixer as in making mineral superphosphates. But bone dust does not behave nearly so well as mineral phosphate under the action of the sulphuric acid. It has already been pointed out, that mineral superphosphates contain free phosphoric acid, which renders them moist to the touch. To this drawback, another is added in the case of bone superphosphate, the sulphuric acid converts the organic matter into a viscous mass, which prevents the drying of the superphosphate.

A multitude of methods have been tried to eliminate this drawback, but the greater number have failed. In this way it has been tried to dry the superphosphate with sand, lignite, ash, and other analogous pulverulent matters. But the addition of all these substances not only diminishes the percentage of nitrogen, but it opens the door to sophistication of all sorts. It has been given up.

Another way of attaining the same object, proposed by Rumpler, was the use of bone black. As this material possesses considerable absorptive power for liquids, it may be successfully used to dry manures with a tendency to remain damp. The bone black is incorporated thus: The bone black is first incorporated with the quantity of sulphuric acid required to dissolve its phosphate, at the same time as that for the bone dust. When the decomposition of the black is finished, the bone dust is incorporated with the mixture. If any insoluble phosphate remains undissolved, it is bone phosphate, which becomes readily soluble in the soil.

If it be desired to increase the amount of nitrogen, the gelatine extract obtained by steaming bones may be added to it. But, so as not to introduce too much water into the manure, care is taken to reduce its volume to a third by evaporation, and to use sulphuric acid of high strength. Finally, it is preferable to secure the drying of the phosphate by only dissolving it incompletely. In that case, only $\frac{2}{3}$ or $\frac{3}{4}$ of the sulphuric acid required for completely dissolving the phosphate is used.

Again, the addition of a little nitrate of soda 1 : 2 per cent considerably accelerates drying.

Bone superphosphate dries spontaneously in the heap, and at the end of a month the reactions of which it is the seat are terminated. It suffices then to pass it through a Carr's crusher, and to sift it to reduce it to a pulverulent form.

Mixture of Bone Superphosphate (*Dissolved Bones*) *and Nitrogenous Matter.*—Bone dust from steamed bones only contains on an average 3 to 4 per cent of nitrogen. It does not contain more than

2 per cent after its conversion into superphosphate. It is small compared with the 15 to 17 per cent of soluble phosphoric acid which accompanies it. Manure manufacturers, therefore, try to increase the percentage of nitrogen by the addition of substances of animal origin.[1] By this means the enormous amount of daily waste from animal sources in large towns can be restored to the soil. The process is as follows: The bones, as they come from the digesters, are mixed still moist with acid of 50° B., and the nitrogenous matter added. These nitrogenous matters are those already studied, but their treatment differs a little from that applied to them when used alone.

Blood.—After coagulating the blood by heat in the manner described further on, it is added to the bone dust in the proportion of 300 lb. of fresh blood to 250 lb. of fresh bones. The bone superphosphate thus obtained is rich in nitrogen, it contains in the dry state 4 to 5 per cent of nitrogen, and 9 to 11 per cent of phosphoric acid; it only contains 0·51 per cent of insoluble phosphoric acid. The bone superphosphate to which blood has been added, dries much better; this latter therefore furnishes a means of obtaining a perfectly soluble powder richer in nitrogen. If it be desired to still further increase the nitrogen and to bring it to 5 to 6 per cent for example, the difference can be got over by an addition of dried blood, meat meal, or an ammoniacal salt.[2]

Horn.—Although horn previously steamed may be easily crushed in the flatstone mill, it is better to add it in the state of flour to the finished superphosphate, because if added before grinding it does not distribute itself so well as blood. Wool dust and analogous waste are preferably treated like leather waste, for they are too bulky to be treated by steam.

Leather Waste.—It has already been observed that ground leather prepared from tanned leather is one of the least active of nitrogenous manures. They are best treated as follows: The leather is charged into a large leaden pan capable of being heated by a double bottom or by a lead coil, and moistened with sulphuric

[1] But in Great Britain the manure then ceases by law to be *dissolved bones* and enters the class of *dissolved bone compounds*, and in this latter class the units of nitrogen and phosphoric acid are paid for at a much lower rate than in pure dissolved bones. From a manufacturer's point of view, therefore, it is better to use these nitrogenous adjuncts in making dissolved bone compounds in which little or no bones are used, the bulk if not all of the phosphates being derived from mineral sources.—Tr.

[2] But here again the addition of so much blood would cause this manure in Great Britain to fall into the class of blood manures; at any rate a manure with only 9 to 11 per cent of phosphoric acid (say 20 per cent of soluble phosphates), and no insoluble phosphates, would never pass muster as a genuine dissolved bone. All these animal substances the British manufacturer combines with mineral superphosphate and sells as dissolved bone compound, or in this case possibly as blood manure.—Tr.

acid of 50° to 60° B., and the whole heated to boiling. The leather rapidly dissolves to form a brown liquid, which is drawn off by a tap a little below the false bottom, and which is used in place of ordinary sulphuric acid to dissolve the bones. This method of treating leather presents great advantages. It enables the manufacturer to preserve all the nitrogen, which would otherwise be lost, as extract. Besides, and it is an important point, the tannin opposed to the decomposition of the leather in the soil is destroyed. Flesh, lungs, livers, spoilt greaves and other waste are dissolved by the acid like leather. The sequel of the treatment is the same as in the case of leather. Greaves are particularly rich in nitrogen. They often give up as much as 10 per cent of fat to the sulphuric acid used to decompose them. If sulphate of ammonia be used to increase the nitrogen content of dissolved bones, it likewise can be dissolved in the sulphuric acid, whilst nitrate of soda can only be added to the finished product. The mixing is then done by aid of the crusher or by the toothed roller mill. Hair, horn, and wool waste are also dissolved in the acid. The solubility of the organic matter is greater in nitrous sulphuric acid than in sulphuric acid alone. For one part of these materials, two parts of nitrous sulphuric acid at 50° to 60° B. are taken, and if there be no nitrous acid at disposal residual sulphuric acid is supplied by an addition of 2 per cent of nitrate of soda.[1]

Animal Charcoal.—Commercial animal charcoal comes almost exclusively from sugar refiners and glucose factories. To purify their juices, the refiners use large amounts of animal charcoal. In the new state, that is to say, freshly calcined, the black possesses a very energetic decolorizing power. But this property is attenuated by use. To revivify the black, and to restore to it, at least partially, its decolorizing and purifying properties, it is fermented, treated by acids, washed, then again calcined without access of air. Thus revivifying operations give rise to an important waste under the form of a fine powder, which is sold as manure. After a series of revivifications, the granular black is itself spent, and revivification is powerless to restore to it its initial properties. Formerly animal charcoal was in current use in sugar works, but within the last fifteen years it has completely disappeared. The refineries alone continue to use it, and consequently it is not so important a manure as formerly. The composition of this product is very variable, according to the methods of manufacture of the sugar refineries. As the char dust (revivification) waste comes always from the surface of the granules of black, and as these parts are the most attacked by the hydrochloric acid used to purify it, it contains an important proportion of carbon, but less phosphate of lime, than the granular black.

[1] See note 1, p. 188.

Moreover, it contains much sand. None the less, it is in much request for the manufacture of superphosphate, because it can be treated without any previous preparation. Spent char contains 25 to 75 per cent of phosphate of lime, 1·5 to 15 per cent of carbonate of lime, and up to 1 per cent of sulphate of lime. Spent char dust contains much less of these substances. As the granular char removes nitrogenous impurities from the saccharine juices, it also contains up to 1 per cent of nitrogen. Some analyses of animal charcoal, both before and after its use in the clarification of syrups, are given in Table LI.

TABLE LI.—ANALYSES OF NEW AND USED AND SPENT BONE CHAR. (PIERRE.)

	Nitrogen. Per cent.	Carbon and Organic Matter. Per cent.	Phosphate of Lime. Per cent.	Carbonate of Lime. Per cent.	Various Constituents. Per cent.
Charcoal, fine, new .	1·12	11·6	73·1	8·0	7·3
,, once used .	1·95	21·1	64·6	6·4	7·9
Charcoal, fine, new .	1·22	11·3	72·2	5·3	10·5
,, once used .	2·83	32·0	53·7	4·9	9·4
,, twice used	3·59	42·2	46·0	3·3	8·5
Charcoal, fine, new .	1·61	11·0	75·6	7·0	13·4
,, once used .	2·54	36·2	52·6	10·0	10·1
,, twice used	3·18	42·5	47·5	4·5	5·2

Bone Ash.[1]—The immense prairies of South America support numerous herds of cattle; 1000 head of cattle per inhabitant can be counted in many of these countries. The animals are slaughtered for their horns, their skins, and their fat. The flesh is rarely utilized for human food. It is left to rot, or even as food for wild animals. The bones are dried and used as domestic fuel and in the tallow smelteries, sugar factories, etc., for other fuel is scarce in these districts. It was in that way that from 100 to 200 years back hillocks of bone ash accumulated near dwellings for which, till a short time ago, no use was found even as a manure. But owing

[1] Bone ash is very hard and difficult to grind, besides it is always wet by absorption of moisture apparently from the air, and is best dried on the engine steam boilers, over which for the time being it acts as a non-conducting composition. Bone ash yields an excellent superphosphate with about 40 per cent of soluble phosphate and 1 per cent of insoluble. It is sometimes a little bit difficult to dry, but it takes kindly to the kiln. The manure manufacturer keenly feels the want of supplies of this most valuable product. A cheap machine that would burn spent char to bone ash cheaply and rapidly would supply a great want and enable spent char to fill the place of bone ash, which it cannot now do, as its colour debars it. Bone ash superphosphates, it is needless to say, never retrogrades.—Tr.

to the enormous extension of the use of chemical manures, the value of these ashes has been better appreciated. They are sold to outward bound ships, who purchase them as ballast. As they are in the pulverulent state, bones are also mixed with them, as in that way they are less cumbersome.

The unceasing demand for this excellent waste by chemical manure factories has diminished the stocks; on the other hand bones are utilized to better purpose, the result being that bone ash has now almost disappeared from the market. Five samples of bone ash analysed by Voelcker had the following composition :—

TABLE LII.—SHOWING THE COMPOSITION OF FIVE SAMPLES BONE ASH. (VOELCKER.)

	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.
Water	4·83	9·91	15·34	3·39	10·30
Organic matter	4·06	1·75	2·03		
Phosphoric acid	35·38	33·89	32·63	38·12	29·56
Lime	44·27	39·53	37·84	44·47	34·48
Lime not combined with phosphoric acid	3·53	3·47	1·92	4·45	1·02
Magnesia	0·97	0·97	1·48		
Alkalis	—	1·39	0·84		
Oxide of iron and silica			0·21	5·67	4·40
Carbonic acid	3·01	0·78	0·84		
Sulphuric acid			0·37		
Sand	6·95	8·31	6·50	3·90	20·24
	100·00	100·00	100·00	100·00	100·00
Phosphate of lime	76·65	73·42	70·46	82·59	64·04

By picking out the big lumps, which consist of almost pure bone ash, a product containing about 85 per cent of phosphate of lime is obtained. The fine powder which contains almost all the sand is, naturally, less rich in phosphate. Bone ash is chiefly used for making precipitated phosphate of lime, according to the method already described. They are worth about £3 per ton. The composition of bone ash corresponds to the following formula :—

$$Ca_3(PO_4)^2 + [Ca_3(PO_4)_2CaOCaHPO_4]$$

but 2 to 3 per cent of CaO are replaced by MgO, K_2O and Na_2O and 4 to 6 per cent of phosphoric acid by CO_2, Cl and F.

Manufacture of Precipitated Phosphate of Lime.—Precipitated or basic phosphate of lime is a bye-product of the manufacture of glue. If hydrochloric acid be poured on fat extracted bones, it

dissolves the phosphoric acid contained therein. An acid solution is then obtained of phosphate of lime, and as a residue the osseous matter, ossein, the gelatine of which is extracted by boiling. Formerly, the acid solution of phosphate of lime was not considered of any value, and to get quit of it, no better outlet could be found for it than to run it into the river. But now the phosphate of lime is recovered by precipitating its solution by caustic lime. Unfortunately, the manufacturers are not careful enough in working; the phosphate of lime which they put on the market often contains 12 to 15 per cent of carbonate of lime, or of caustic lime, and a large proportion of chloride of lime [? calcium chloride], which renders it less fit for manure manufacture. The analysis of one of these products furnished the following results :—

TABLE LIII.—ANALYSIS OF PRECIPITATED PHOSPHATE OF LIME.

	Per cent.	
Water and organic matter	26·20	of which nitrogen, 2·68 per cent.
Phosphate of lime . .	53·50	phosphoric acid, 28 per cent.
Phosphate of magnesia .	2·17	
Phosphate of oxide of iron	5·30	
Sulphate of lime . .	2·07	
Carbonate of lime . .	0·88	
Chloride of calcium . .	3·50	
Lime	0·46	
Potash	0·21	
Soda	0·29	
Insoluble	5·42	
	100·00	

Lately the manufacture of phosphate of lime in glue factories has been perceptibly improved, and the product put on the market is of better quality. Precipitated phosphates of lime are also made from phosphates unfit for making superphosphates, and from bone ash, but in these cases the impurities contained in the raw material, such as oxide of iron and alumina, are likewise dissolved, and remain in the product.[1]

The manufacture of precipitated phosphate of lime consists, as already mentioned, in decomposing phosphate of lime by hydrochloric acid, and in separating the chloride of calcium after the equation—

$$Ca_3(PO_4)^2 + 2HCl = 2CaHPO_4 + CaCl_2$$

The phosphoric acid is precipitated from its solution by milk of lime. The neutralization must be done with care, for it only

[1] The author gives no explanation here of why he should select the purest material, such as bone ash, to make precipitated phosphate, and then go to the opposite extreme to select the most impure, so impure that they cannot be used to make even ordinary superphosphate. The analysis given is certainly not of one made from bone ash. The phosphate of iron content again is too high to be made from bones even if indicated by the 2·68 per cent. of nitrogen.—Tr.

requires a slight excess of lime to form an insoluble phosphate—one part P_2O_5 requires 0·4 of CaO, as the following equations show :—

$$CaH_4(PO_4)^2H_2O + CaO + H_2O = Ca_2H_2(PO_4)_2 2H_2O$$
$$CaH_4(PO_4)^2H_2O + 2CaO = Ca3P_2O_8 3H_2O$$

To prepare the acid phosphoric solutions, a wooden vat is fitted with a mechanical agitator also of wood. No mechanical agitator is required working with bones. The bones are covered completely by an 8 per cent solution of hydrochloric acid, and left in contact for two to three days. All the mineral matter is dissolved, whilst the ossein, a white soft substance, remains undissolved. The benzine fat-extracted bones decompose more easily than steamed bones. The decomposition is ascertained to be finished when a hollow bone placed at the surface as a sample is soft and supple, and shows well the characteristics of swollen ossein. The solution is then run off through a tap in the bottom of the vat, the ossein is washed with the smallest possible amount of 4 per cent hydrochloric acid, and the liquid is collected in a tank. The

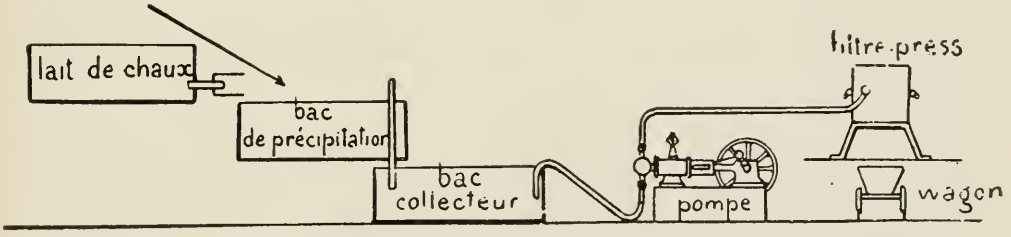


Fig. 37.—Plant for Manufacture of Precipitated Phosphate of Lime.

Lait de chaux = Milk of Lime. *Bac de précipitation* = Precipitation Vat. *Bac collecteur* = Collecting Vat. *Pompe* = Pump.

wash water is used afterwards to dilute the strong hydrochloric acid, that is why a more methodical extraction is not pursued. As to the quantity of hydrochloric acid, a little more than the theoretical quantity calculated on the lime must be used. When the phosphate is finally ground, solution is effected in ten to fifteen minutes; it is pumped into a filter press by means of a pump with lead armature. The phosphatic solution is collected in an open lead-lined vat, not too deep, in which it is neutralized by milk of lime. To precipitate the $Ca_2H_2PO_4$, milk of lime, in quantity just sufficient to neutralize the free HCl, is added, the HCl used, and the phosphoric acid content of the substance must be known, then one molecule of CaO for each molecule of $CaH_4P_2O_8$. For this purpose there is installed on a level with the top of the neutralizing vat, a second lead-lined vat fitted with a tap 15 cm. above the bottom, in which a milk of lime is prepared, which is run into the neutralizing vat, care being taken to stir the mixture in the latter. To make sure that enough milk of lime has been added, a

sample is filtered from time to time, and tested with molybdate, or phenol phthalein in the case of $Ca_3P_2O_8$. To work in a continuous fashion, two neutralizing vats are installed below the milk of lime vat; the latter is then fitted with two delivery pipes, which are closed when need be by a cork stopper. When the contents of one of the vats is being neutralized, the second is being filled with phosphate solution from the filter press. If excess of milk of lime be added, it is easy to remedy it by running in phosphate solution from the other vat. Finally, there is installed below the neutralizing vats a pit or collecting vat into which the neutralized solution runs through a pipe fixed in the bottom of the two aforesaid vats. To neutralize the solution as exactly as possible, a milk of lime of 15° B. = about 16 per cent CaO is used, of which enough is added for the solution to remain faintly acid; when the liquid is clarified it is decanted from the precipitate, and the neutralization finished apart. The first precipitate is $Ca_2H_2(PO_4)_2$, the second is partly $Ca_3(PO_4)^2$. From the collecting vat the neutralized material is drawn by a suction and propelling pump and forced into a Phillippe's washing filter press; the precipitate is freed from adherent calcium chloride by washing with water, followed by steam washing. The precipitate filters well. The cakes extracted from the filter press are dried at a temperature of 60° C. (140° F.); at the maximum, best in the steam drying machine.

They are converted into a fine friable powder containing 30 to 40 per cent of P_2O_5. At a higher temperature the $Ca_2H_2(PO_4)$ becomes slightly soluble. (Formation of $P_2O_7Ca_2$.) When local facilities lend themselves to it, the vats are installed in such a fashion that they run from the one to the other. The last filter press for the precipitate is then at a sufficient height for the cakes to fall directly into a truck, which conveys them to the drier. The precipitated phosphate is soluble in a solution of citric acid. The manufacture of this product has been the object of numerous researches and several patents.[1]

A precipitated phosphate manufactory requires:—

1 ball mill.
2 agitating vats.
10 filter presses of 250 litres (55 gallons).
5 pumps.
2 lime vats with stirrers.
2 collecting vats.
1 steam dryer.
4 pits with agitator, 2 metres × 2½ metres.

[1] The whole subject was covered and exhausted, the filter press excepted, by the numerous British patents of the 'sixties and 'seventies.—Tr.

CHAPTER XI.

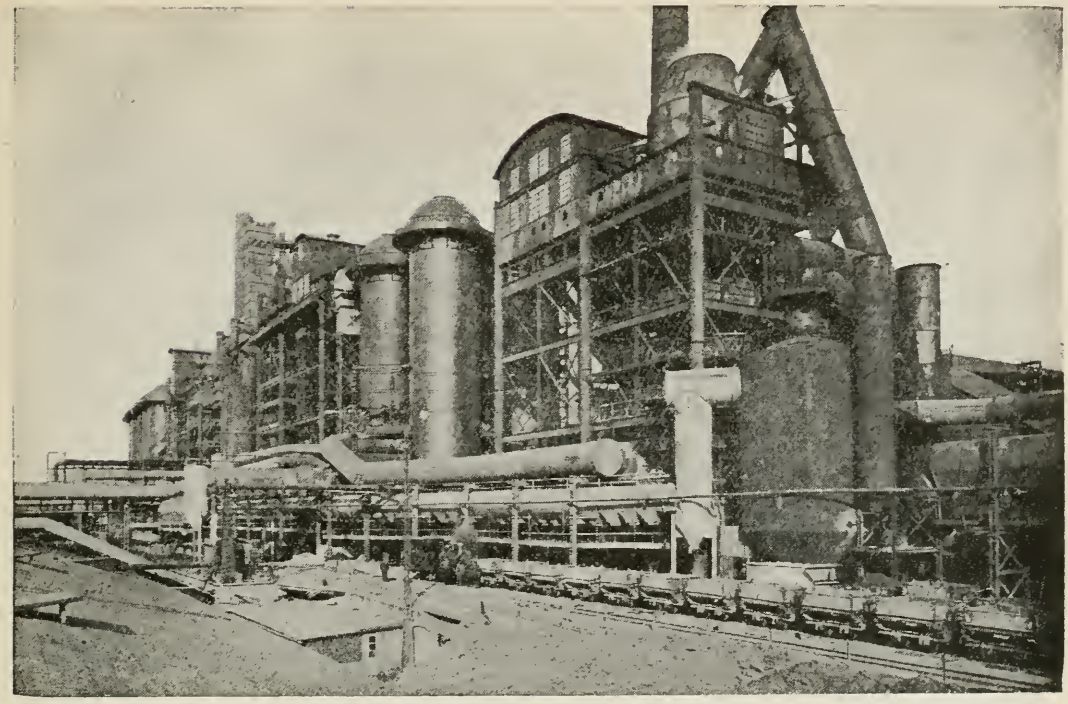
MANUFACTURE OF BASIC SLAG.

A Retrospective Glance.—In the early days of the application of the Thomas and Gilchrist process, the basic slag from the dephosphorization formed a cumbersome ballast. Gradually the idea came to use it as a manure, but agronomists did not, at first sight, come across the true method of utilizing this waste. They imagined, by analogy with mineral phosphates, that it would be necessary to cause it to undergo a similar conversion as the latter. But looking to the nature of the slag itself, one would not dream of converting it into superphosphate. Precipitated phosphate of lime was therefore made from it by Scheibler's patent, which was put on the market as *Thomas precipitate* either alone or mixed with nitrate or ammonia. This precipitate, prepared by the Fertilitas Company, tested 32 to 35 per cent of phosphoric acid, of which 80 to 90 per cent was soluble in citrate. In May, 1885, The Anglo-Continental Co. took up the sale of the new product, but in spite of the support of this powerful company, Thomas precipitate did not have great success, looking more especially to its high price. At the same time, G. Hoyermann and Heinrich Albert commenced researches to determine the fertilizing value of the basic slag in its natural state. Hoyermann engaged a certain number of farmers of the province of Hanover to spread finely ground basic slag on marshy lands and meadows. On his part, Heinrich Albert, who had for a long time recognized the solvent rôle of the acids elaborated by the roots of plants, devoted several years to the study of the action exerted on phosphates by weak solvents. He remarked that peat finely ground and kept very moist constituted a somewhat energetic solvent for phosphate. He applied his methods to basic slag and obtained excellent results. In 1885 the agricultural station of Darmstadt entered the same field, and in its turn made cultural experiments with basic slag, thanks especially to the financial support of the syndicate of German manure manufacturers. These experiments were continued for several years, and in 1889 Dr. Paul Wagner published the results obtained. Nevertheless, manure manufacturers themselves remained sceptical, and only two of them consented to deal with the metallurgical firms for the supply of basic slag. Their hesitation will be readily under-

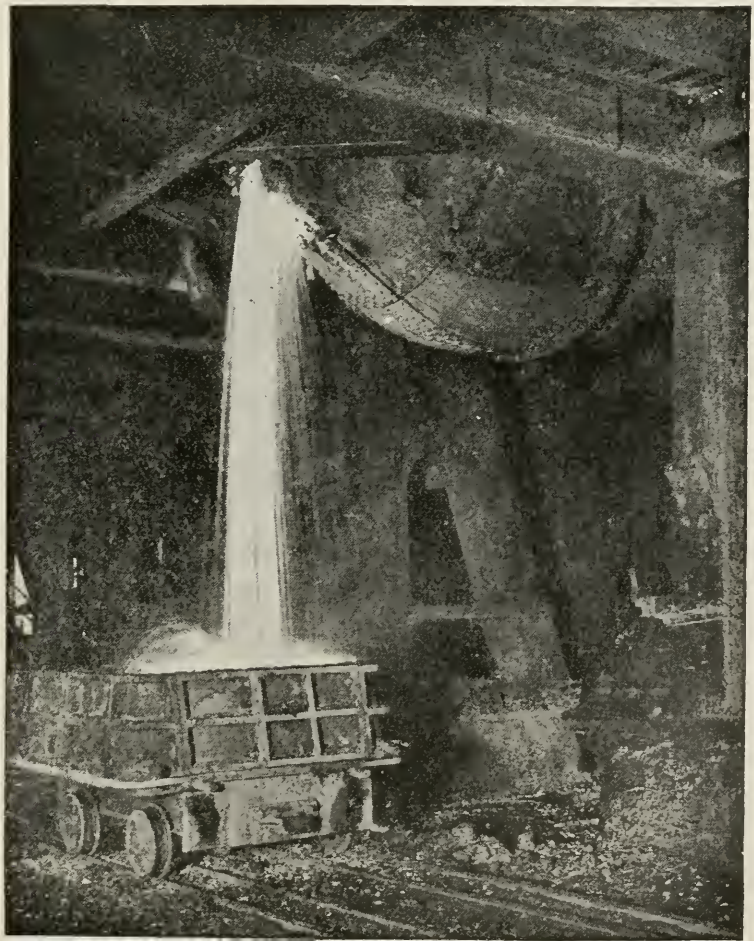
stood if one thinks of the great difficulties which they had to surmount, from a technical point of view, to reduce the slag to a fine powder, and to obtain with a material at that time of very varying strength a marketable product of uniform strength. When, later on, the solubility in citric acid was adopted as the method of determining the fertilizing value of basic slag in powder, it was again Hoyermann who, working from his own data, suggested the addition of silica in the converter, as a means of considerably increasing the solubility of the phosphoric acid. It is thus that, through apparently insurmountable difficulties, basic slag became a precious source of phosphoric acid for agriculture. Its comparative cheapness, its content of lime and silica, and the good results which they give on meadows, peaty soils, sandy soils poor in lime, have caused basic slag to be used in all intensive culture countries. It no longer forms, as previously, a useless and cumbersome ballast, but a product of great fertilizing value, the consumption of which increases from year to year.

Origin of Basic Slag.—Up to a comparatively recent epoch, good steel could only be obtained by using ores exempt or almost exempt from phosphorus. A proportion of 0·25 of phosphorus sufficed to render the iron brittle in the cold. These sort of ores had become more and more rare, whilst there existed abundant deposits of phosphorous ore. The attention of metallurgists was, therefore, bound to turn in the direction of the latter, and it was necessary to try to utilize them.

It is to two young Englishmen, Thomas Gilchrist (?) and Percy Gilchrist, to whom in 1879 the honour of this discovery, which was to revolutionize the manufacture of steel, is due. It did not enter into ordinary practice until after five or six years of efforts, varied tentatives and numerous and delicate trials. It is now the basis of the manufacture of the greater part of steel. The Thomas process, as it is called, has a double advantage: it enables an excellent steel free from phosphorus to be obtained whilst utilizing the phosphorus ore; and on the other hand it gives as a secondary product a fertilizing material, the use of which, in agriculture, has assumed a rapid and considerable extension. Let us now examine rapidly the manufacture of the cast-iron, then that of the steel which yields the slag. The ore conveyed to the ironworks is smelted in blast furnaces which reach to about 65 feet in height by 20 feet in width; it is there laid alternately with layers of coke, and there is added, according to the nature of the mineral, calcareous or silicious matter which forms what is called the *castine* or *erbue*. The object of this lining is to deprive the mineral of any argillaceous or calcareous gangue present, and to obtain finally, in consequence of the de-oxidation and of the partial carburation of the ore, as a useful product cast-iron, and as residue, a lighter substance floating on the top



A Steel-Works and its Blast Furnaces.



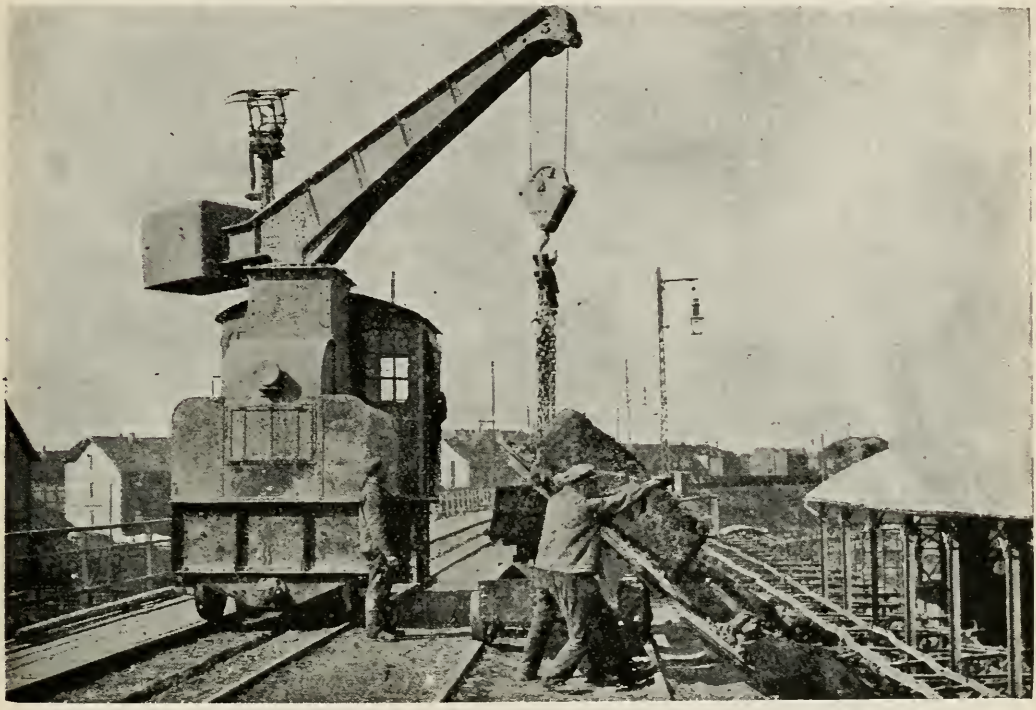
constituting the slag, which contains the major part of the impurities combined with the *castine*.

As to the gases which escape in consequence of this de-oxidation, they are collected and their heat utilized, either to heat the air which enters the blast furnaces to a temperature of 750° C., or to produce the steam necessary to drive the blowing engine, or finally to produce electricity. The charging of the blast furnace is done continuously through the top, and its discharge through the bottom (about every six hours). The temperature of the lower zone where the molten iron frees itself by difference of density from its floating impurities is about 1200° C. The slag is utilized industrially for making bricks, cement, etc. Let us see what becomes of the cast-iron, which at this point is still phosphorusetted, as the following analysis taken as an example shows:—

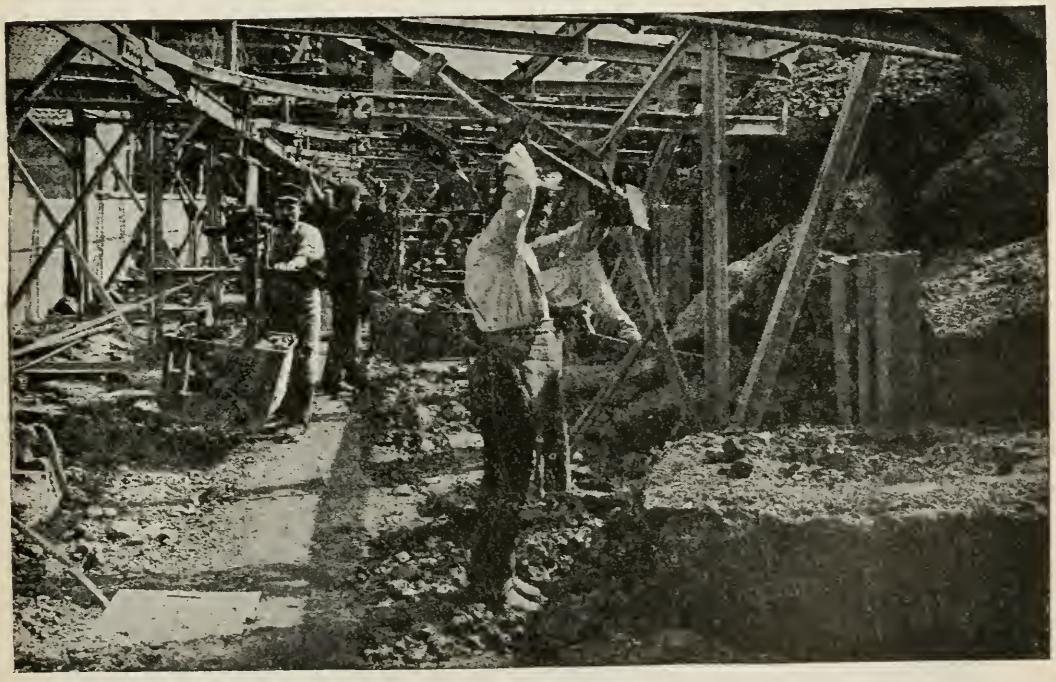
TABLE LIV.—ANALYSIS OF CAST-IRON SHOWING PHOSPHORUS CONTENT.

	Per cent.
Iron	91·20
Carbon	3·60
Phosphorus	2·75
Magnesia	3·20
Silicon	0·25
	100·00

The conversion of the cast-iron into steel is done in special pear-shaped appliances, movable round a horizontal axis, and made of steel lined with refractory stone. These appliances, termed convertors, are in the Thomas process lined in the interior with lime and magnesia. They are open on the top and pierced in the lower part by holes through which air at a high temperature can be blown. To charge them they are turned around on their axes to an angle of 90° and the liquid cast-iron is run in through the upper opening. Then the pear is raised at the same time that air is driven through the lower holes at a sufficient pressure for the fused metal to remain in the convertor and not pass through the holes. Under the influence of the high temperature prevailing in the convertor, and of the air injected, the silicon, the sulphur, the phosphorus are burnt at the same time as a part of the carbon. The heat which is disengaged inside the convertor is such that the metal, which had at the moment of its introduction a temperature of 1200°, rises to 2100°, all within thirteen minutes. The phosphorus is oxidized and is converted into ortho-phosphoric acid, and as it is in the presence of excess of lime, it combines in a peculiar form tetrabasic phosphate associated with calcium silicate and forms what is called basic slag. When the operation is finished, which is ascertained by the appearance of the gas given off from the top of the convertor, the latter is



Unloading Basic Slag in Blocks.

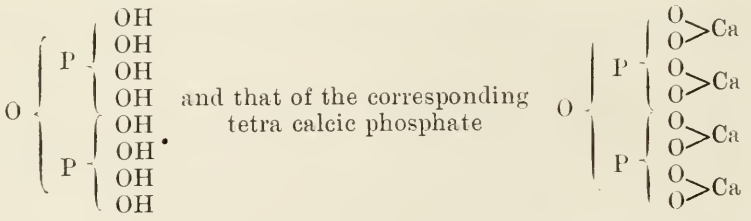


Preliminary Breaking-up of Basic Slag.

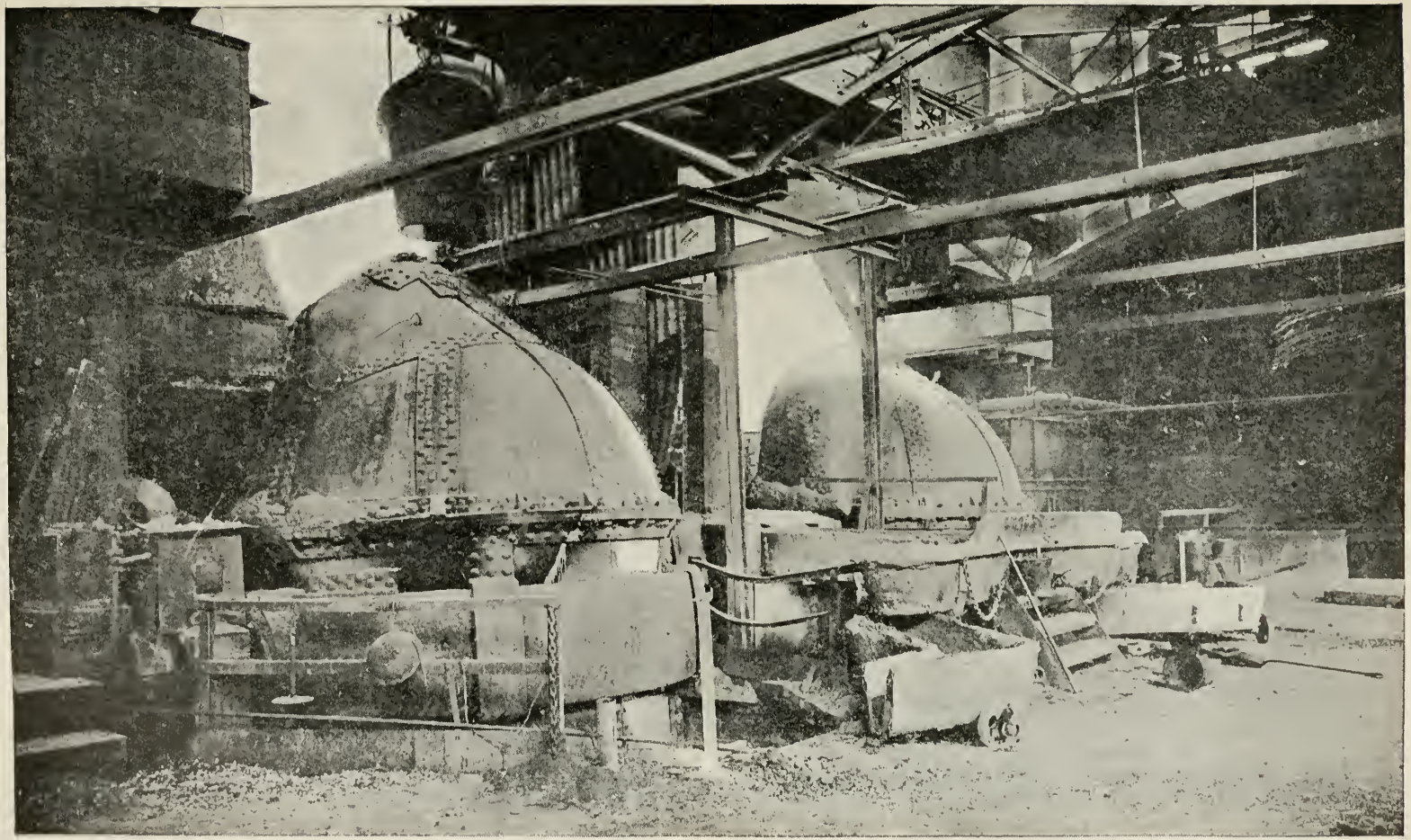
inclined on its axes, and the current of air is suspended and the liquid slag floating on the cast-iron is poured into a metallic truck forming a case and containing a certain quantity of finely pulverized fused silica. The weight of the slag in one of these trucks may reach 4½ tons and even more. The whole is conveyed on rails to the spot where it is to be handled, and after cooling, facilitated by sprinkling with water, the mass is removed from the truck and discharged into a crushing shed.

The Nature of Basic Slag.—Basic slag occurs as more or less bulky blackish fragments, porous, strewn with tablets of steel and of great density. It slakes in the air; the caustic lime absorbs moisture and carbonic acid and the ferrous oxide oxidizes. Contrary to an opinion expressed at first, the absorption of carbonic acid decomposes the tetrabasic phosphate. In the porous part of the slag translucid crystals are met with, rhombic tablettes, hexagonal prisms, and monoclinic needles 10 to 15 mm. long, of a grey, brown or blue (produced by FeO) colour intermingled or ranged symmetrically. These crystals consist principally of tetrabasic phosphate of lime, $Ca_4P_2O_9$. They have been the object of very interesting researches, the principal points of which will now be summarized.

Tetraphosphate of Calcium.—$Ca_4P_2O_9$ may be regarded as being the neutral salt of an octobasic diphosphoric acid $P_2O(OH)_8$ not yet produced in the free state, the structural formula of which would be the following :—



The presence of this compound in basic slag has been determined by a great number of scientists, so that there can be no doubt as to the soundness of the hypothesis enunciated above. The small blue crystals which are found in the paste, and more especially in the *geodes* of the slag, were studied from a crystallographic point of view by A. Richard, who refers them to the orthorhombic system, and notes amongst their properties a strong double refraction and a very marked dichroism, the same crystal appearing colourless or a beautiful cobalt blue in two rectangular positions. Prof. Carnot at this time termed these crystals silico phosphates of lime and gave them the formula $P_2O_5SiO_2 5CaO$. In the same year Hilgenstock examined the other crystals. He found in the scoriæ of these, crystals in the form of thin rectangular tablets colourless or of a light brown according to the thickness. He placed them in the rhombic system.



Thomas Convertor at Work.

He recognized their composition as that of a tetrabasic phosphate of lime $Ca_4P_2O_9$ or P_2O4CaO. This analysis having given rise to certain discussion, it was again taken up by Carnot on the one hand and on the other by Stead and Ridsdale. They found :—

TABLE LV.—ANALYSES OF CRYSTALS OF TETRABASIC PHOSPHATE OF LIME FOUND IN BASIC SLAG.

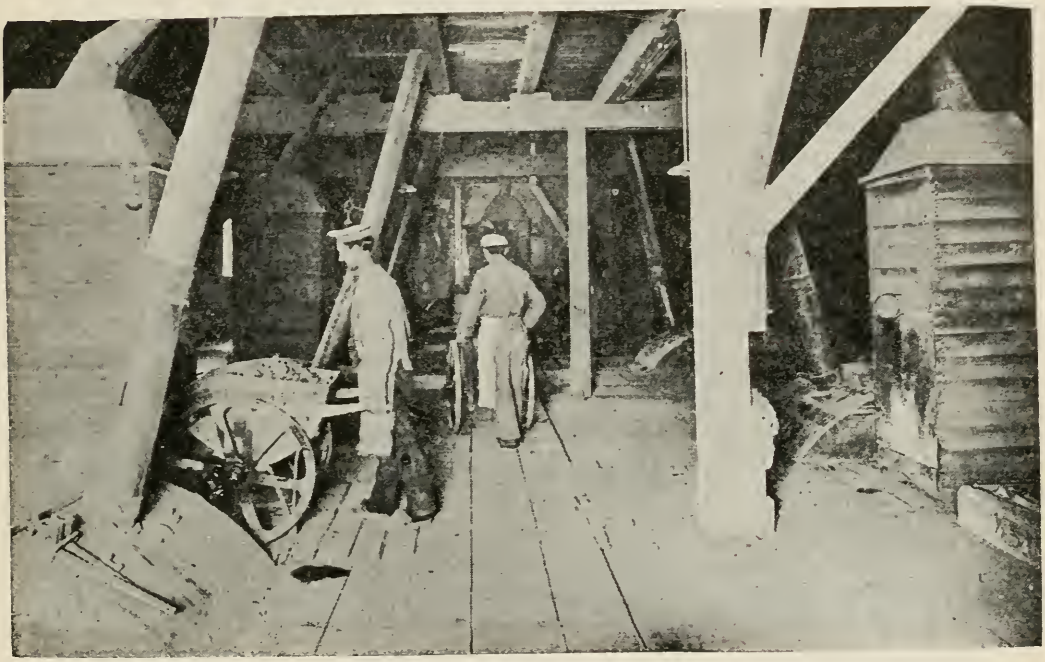
	Carnot. *Per cent.*	*Stead and Ridsdale.* *Per cent.*
Phosphoric acid	37·67	38·044
Silica	0·74	traces
Lime	59·54	60·206
Magnesia	traces	0·828
Ferrous oxide	1·44	0·100
Alumina	0·37	
Vanadium oxide	—	0·722
Sulphur	—	0·150
	99·76	100·050

These results confirm the formula of tetrabasic phosphate of lime, besides the two forms of crystals described. There were likewise found brown or almost colourless needles of a hexagonal form. Their analyses give the following figures :—

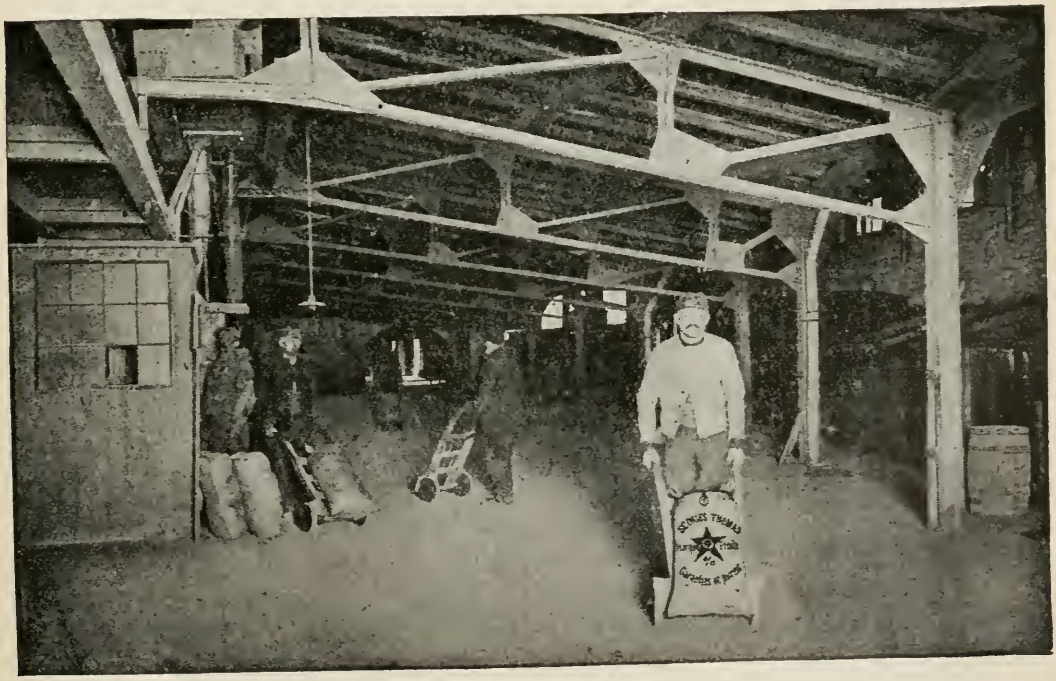
TABLE LVI.—ANALYSES OF HEXAGONAL CRYSTALS FOUND IN BASIC SLAG.

	Hilgenstock. Per cent.	Bucking and Link. Per cent.	Head. Per cent.
Phosphoric acid	34·94	36·77	33·707
Silica	3·24	3·81	3·900
Lime	57·55	53·51	53·536
Magnesia	—	0·40	0·486
Manganous oxide	—	—	0·790
Ferrous oxide	4·00	2·22	1·286
Ferric oxide	—	1·78	4·857
Alumina	—	1·09	—
Vanadium oxide	—	—	1·343
Sulphur	—	traces	0·460
	99·73	99·58	100·365

The differences which exist between these analyses are explained by the difficulty which there is in isolating the crystals from the impurities which remain partially adherent thereto. Stead and Ridsdale have in fact distinguished two other varieties of crystals, black flat needles, some of which are magnetic while the others are not so. They have found the composition to be as follows :—



Feeding Basic Slag into Ball Mills. (View from above.)



Handling of Ground Basic Slag. (Bagging-up in 100 kilos (220 lb.) lead-sealed bags.)

TABLE LVII.—ANALYSES OF BLACK NEEDLES, MAGNETIC AND NON-MAGNETIC, FOUND IN BASIC SLAG.

	Magnetic.	*Non-magnetic.*
Lime	39·088	44·730
Magnesia	1·297	0·936
Alumina	6·400	9·700
Ferric oxide	33·857	35·657
Ferrous oxide	8·100	—
Manganous oxide	1·748	1·023
Chromium sesquioxide	5·980	4·200
Vanadium oxide	2·656	2·223
Silica	1·100	0·900
Phosphoric acid	traces	0·740
	99·826	100·109

According to these authors, these crystals would therefore consist chiefly of ferrite and of aluminate of lime. The analyses of the blue crystals give :—

TABLE LVIII.—ANALYSES OF BLUE CRYSTALS FOUND IN BASIC SLAG.

	Carnot. Per cent.	Hilgenstock. Per cent.	Bucking and Link. Per cent.
Phosphoric acid	29·65	30·85	31·19
Silica	12·42	9·42	9·47
Lime	53·20	57·60	57·42
Magnesia	traces	—	traces
Ferrous oxide	1·80	2·94	0·95
Manganous oxide	traces	—	—
Alumina	2·76	—	1·13
Sulphur	—	—	traces
	99·83	100·81	100·16

These figures correspond exactly with the formula—

$$8P_2O_5,\ 8SiO_2,\ 36CaO,\ FeO,\ Al_2O_3$$

By replacing small quantities of oxide of iron and alumina by equivalent amounts of lime, a more simple formula is arrived at, P_2O_5, $SiO_2 5$, CaO, which may also be written—

$$P_2O_5,\ 3CaO + SiO_2,\ 2CaO$$

Hilgenstock and Carnot have examined the order of formation of the crystals, and both have come to the same conclusions.

The first crystals which are formed appear to be the rectangular tablets on which afterwards come the brown hexagonal needles. It is only later that the rest of the slag, becoming richer in silica, isolates the blue and brilliant crystals. These are superposed by the

brown and black needles. The order of appearance seems, therefore, regulated both by the gradually decreasing temperature and by the composition of the bath of slag which becomes richer in silica and less rich in phosphoric acid. Cultural experiments have been made with the object of examining the action of certain elements of basic slag. They will be examined further on.

Solubility of Basic Slag.—Formerly basic slag was regarded as a product of no value, because there was no means of dissolving it, owing to its high percentage of iron and lime; neither any more did any one dream of utilizing it in agriculture, because they knew very well that raw phosphates possess no direct fertilizing value. Scheibler suggested the preparation from the basic slag of a precipitate, German patents 24,130 and 25,020. For that purpose he treated 100 parts of basic slag in powder with 120 to 150 parts of hydrochloric acid and precipitated the phosphoric acid by milk of lime. Francke recommended the decomposition of basic slag by magnesium chloride, German patent 27,106, and to convert the phosphoric acid into phosphate of magnesia. G. Meyer, on his part, signalized the treatment of fused basic slag with its own weight of acid sulphate of potash. The silicate of potash ought to give still better results. The object of all these treatments was to facilitate grinding on the one hand, and to increase the fertilizing value of the basic slag, by dissolving it, on the other hand. But up till now no steel-works has felt it advisable to resort to these mixtures, though the manipulations which they suppose in no way hinder the progress of the manufacture. The last-mentioned process would, however, appear to have the advantage of suppressing the unpleasant part which the spreading of basic slag now presents. All the processes which have been suggested to increase the fertilizing value of this manure need not be dwelt upon here, besides they have not been adopted in actual practice. It was first of all asserted that the phosphoric acid of basic slag, looking to its origin, was less soluble than that under any other form, but V. Reis and Arens, amongst others, showed that phosphoric acid combined with the silicate of lime was soluble in carbonated water. It is from these researches that the use of basic slag in agriculture dates. The results obtained by these two are given in the following table (p. 209); the figures of this table show the great solubility of basic slag in water saturated with carbonic acid compared with that of the other phosphates. The decomposition of tetraphosphate of lime takes place according to the equation—

$$P_2O_9Ca_4 + CO_2 = CaH_4(PO_4)^2 + 3CaH_2(CO_2)^2 + H_2O$$

There is thus formed an acid phosphate of lime such as is also found in superphosphates. The solubility of basic slag in citric acid and in citrate of ammonia and also in tartaric, acetic and oxalic

acid has been the subject of profound researches by E. Jensch which are of so much the greater interest because the solubility in the same solvents of the calcareous silicates always present in basic slag were determined at the same time. Jensch's researches were made on basic slags of very different ages and origins for comparison. He determined the solubility of both Podolia phosphorites and Somme phosphate. The method pursued consisted in mixing each time 1 grm. of the substance with 150 c.c. of the solvent concentration 1 in 20, exposing the mixture during twelve hours to a temperature of 50 to 70° C., then to dilute the solution in 100 c.c. of water. The liquid was heated to boiling, filtered to separate the insoluble, ignited, and the phosphoric acid titrated in the usual way. The difference in the contents of the different elements in the residue on the one hand and the raw material on the other hand, gives the quantities dissolved by the organic acid. Jensch operated on eleven samples of basic slag reduced to a fine powder (1 to 11); three samples of crystals of raw slag (12, 13, 14). A sample of Podolian phosphorite (15) and a sample of Somme phosphate (16). The following table (p. 210) gives on the one hand the content of the substances examined in silica, lime and phosphoric acid, on the other hand, the quantities of phosphoric acid dissolved by the different solvents, also the centesimal amounts remaining undissolved in the residues. These figures show that the phosphoric acid behaves perceptibly in the same manner in basic slags containing more than 18 per cent of that acid as in those which only contain it in small proportion. Thus it is that rich basic slags in current use in agriculture only contain 0·13 to 0·20 insoluble in citric acid, whilst low strength basic slags only contain 0·04 to 0·14 per cent. The solubility in oxalic acid yields equally concordant results. That acid dissolves tetracalcic phosphate and only gives a slight residue of insoluble which consists probably of tricalcic phosphate. The crystals separated from the basic slags (12, 13, 14) show a still greater solubility. The other organic acids used in this series of experiments act less energetically on the phosphates of basic slag; however, here again a certain uniformity can be established between the solubility of the different phosphates.

The silicates, which are highly basic, although of a composition often very variable for the same origin, are distinguished by their solubility in the organic acids, a property which is absolutely awanting in the silicate compounds of the natural phosphates, phosphorite, apatite, etc. It follows that the degree of solubility of the phosphoric acid of basic slag depends on the nature of the calcareous silicates contained therein. Again, if the fragments of basic slags show a uniform crystalline structure, that is to say if they are deprived of agglomerations of caustic lime, which are sometimes observed therein, their content in free lime will be very small and will

TABLE LIX.—SOLUBILITY OF BASIC SLAG IN WATER SATURATED WITH CARBONIC ACID.

	Content of			Quantities dissolved by 10 litres of water saturated by CO_2			Comparative Solubility.		
	SiO_2 Per cent.	P_2O_5 Per cent.	CaO Per cent.	SiO_2 Per cent.	P_2O_5 Per cent.	CaO Per cent.	SiO_2 Per cent.	P_2O_5 Per cent.	CaO Per cent.
Basic slag I.	2·57	18·30	48·68	1·51	4·19	19·37	58·8	22·9	39·8
,, II.	5·20	15·07	48·82	3·15	5·66	24·84	50·9	37·4	51·0
,, III.	2·85	21·30	48·36	2·11	7·55	27·85	74·0	35·5	57·5
,, IV.	4·05	18·33	50·35	2·27	6·81	24·19	56·0	37·5	48·0
,, V.	7·67	16·32	47·98	4·22	7·89	24·54	56·3	48·1	51·1
,, VI.	6·93	15·74	48·15	3·55	4·50	25·08	51·2	28·7	52·0
,, VII.	5·54	24·00	46·35	3·05	7·59	19·36	86·1	31·6	41·7
Shell slag	18·15	13·47	44·10	4·99	3·45	15·17	27·4	25·5	34·4
Prepared slag	6·58	24·95	51·25	4·07	7·79	21·00	61·8	31·2	40·9
Scheibler's precipitate	8·02	33·36	31·10	0·62	7·36	9·37	7·7	22·0	30·1
Hoyermann's precipitate	5·70	14·93	34·05	1·29	4·96	19·96	22·7	33·0	58·5
Bicalcic phosphate of lime	—	51·09	41·03	—	8·57	6·95	—	16·8	16·8
Tricalcic phosphate of lime	—	43·26	51·45	—	5·41	7·04	—	12·5	13·6
Tetracalcic phosphate of lime	—	36·85	62·70	—	15·52	33·27	—	42·1	53·0
Degreased cattle bones	—	25·23	32·75	—	7·19	9·65	—	28·5	28·9
Bone ash made from above bones	—	41·71	55·75	—	2·29	3·29	—	5·5	5·9
Phosphorite	1·77	32·00	45·36	0·10	1·00	1·67	5·7	3·1	3·8

TABLE LX.—SHOWING THE RESULTS OF JENSCH'S RESEARCHES ON BASIC SLAG.

		Commercial Basic Slags.						Commercial Basic Slags.				Crystals.		Phosphorites.		
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Silica	4·41	5·03	10·04	14·15	22·41	10·08	20·77	6·94	19·49	8·98	9·39	2·24	12·14	3·58	2·18	3·61
Lime	54·17	56·03	49·1	48·83	40·04	49·45	39·71	48·07	42·25	44·02	48·63	60·10	62·62	60·81	48·67	50·22
Phosphoric acid	18·21	19·64	18·03	16·26	13·23	16·86	12·41	40·32	16·28	14·83	15·18	36·40	24·81	27·10	38·20	35·29
Of which soluble in :—																
(*a*) Citric acid	18·08	19·60	17·98	16·24	13·15	16·78	12·32	20·30	16·22	14·80	15·04	36·39	24·77	27·08	0·16	0·2
(*b*) Tartaric acid	3·96	4·27	3 91	3·84	2·22	3·63	3·02	6·41	2·87	2·45	2·23	6·49	5·06	5·97	0·02	0·03
(*c*) Acetic acid	5·33	6·21	4·11	4·37	2·46	3·88	3·10	8·12	3·07	2·06	2·64	18·80	17·32	9·17	—	trace
(*d*) Oxalic acid	18·11	19·52	17·94	16·05	13·06	16·70	12·23	20·06	16·20	14·73	15·06	36·37	24·80	27·03	trace	—
(*e*) Neutral ammonium citrate	3·78	3·24	4·09	3·66	1·88	4·01	2·97	3·14	2·90	2·65	3·02	16·72	16·24	5·83	—	—
Insoluble per cent of total phosphoric acid (*a*)	0·71	0·20	0·27	0·12	0·60	0·48	0·73	0·10	0·31	0·20	0·92	0·03	0·16	6·07	99·58	99·38
Insoluble per cent of total phosphoric acid (*b*)	78·25	78·26	77·76	76·38	83·22	78·47	75·66	68·99	82·37	83·48	85·19	82·17	79·60	77·97	99 95	99·92
Insoluble per cent of total phosphoric acid (*c*)	70·73	68·88	77·20	73·12	81·41	76·39	75·02	60·04	81·14	86·10	82·49	48·35	30·19	06·16	—	—
Insoluble per cent of total phosphoric acid (*d*)	0·55	0·61	0·50	1·28	1·28	0·95	1·45	1·28	0·49	0·68	0·69	0·08	0·04	0·25	—	—
Insoluble per cent of total phosphoric acid (*e*)	79·24	83·53	77·31	77·48	85·79	76·21	76·07	84·56	81·57	82·13	80·10	54·07	34·54	78·49	—	—

rarely exceed 2 per cent. But the more these calcareous agglomerates are present, the higher will be the free lime content. It is true that that lime not being combined chemically with the phosphate, but in a state of simple mixture, and up to a certain point as impurity, cannot exercise any influence on the solubility of the phosphoric acid in the soil, for those bodies can only act as solvents which are of a nature to modify the chemical nature of another body. The neglect of this principle has led some authorities to ascribe to the uncombined lime in basic slag an importance which it absolutely does not possess. What determines the solubility of the phosphoric acid in basic slag is the strongly basic calcareous silicates with which it is combined.

The magnesia likewise forms with the phosphoric acid a tetraphosphate, but the solubility of this body considerably exceeds the solubility of the corresponding calcareous compounds. Basic slags rich in magnesia dissolve much more rapidly in organic acids than those in which magnesia is absent. The action of citric acid on the slags shows that the magnesia is chiefly combined with the phosphoric acid and not with the silica. It is perfectly possible, and in all cases very likely, that the action of phosphoric acid of basic slag in the soil depends, in the first instance, on the presence of these silicates. We would thus be confronted with double compounds, phosphates, and silicates of calcium which are dissolved with the greatest facility by water containing carbonic acid, hence, therefore, the solution of the phosphoric acid and its absorption by plants follows. It has been remarked, in fact, that the most active basic slags are always those with a high percentage of silica. Steel works, therefore, possess a very simple and in no way costly method of increasing the solubility of basic slag in citrate; it suffices to add hot sand to it in the convertor, the sand melts like butter, is converted into silicic acid and combines with the phosphate of lime to increase its solubility. It is clear, in that case, that lime should not be deficient in the slag. Silica, therefore, plays a very important rôle in the basic slag. $CaSiO_4$ converts the slightly soluble phosphate of the slag into $Ca_4P_2O_9$ according to the following equations :—

$$Ca_3(PO_4)^2 + Ca_2SiO_4 = Ca_4P_2O_9 + CaSiO_3$$
$$Fe_3(PO_4)^2 + 2Ca_2SiO_4 = Ca_4P_2O_9 + Fe_3Si_2O_7$$

The introduction of an excess of silica helps to decompose $Ca_4P_2O_9$ afresh. There exists in Germany a factory which makes basic slag with 24 per cent of phosphoric acid according to Scheibler's patent, German patents 34,416 and 41,303. A little less lime than that required by the complete dephosphorization of the cast-iron is added to the convertor, and the slag so obtained run out. The remainder of the lime is then added, and the low strength slag which results is used as a reducing substance in the convertor. To increase the strength of the slag in phosphoric acid, phosphated chalk may also

be added to the cast-iron in lieu of lime, eventually mixed with sand. Fused phosphatic chalk has the same solubility as the best slags. ($CaCO_3$ melts at 1000° C., the phosphate at 1900° C.)

Crushing of Basic Slag.—In the beginning of the basic slag industry it was very difficult to crush. Cylindrical crushers and flatstone mills were used at that time. But as the basic slag is mixed with grains of steel of larger or smaller size, the plant was rapidly worn out. Attempts were then made to eliminate the pieces of iron in the basic slag by means of magnetic separators. But these methods did not give good results; the separation of iron was incomplete and the cleaning of the machines involved frequent stoppage. From 1888 mills with forged steel balls, the wear of which is very slight, have been used. Ball mills, moreover, almost entirely do away with dust, owing to the installation of a special chamber intended to collect it, and of a draught chimney which draws it thereto. The hot air entering the draught chimney entrains the dust formed in the crusher; about 1 per cent of dust is got for 100 of fine powder. When fans were used—useless with the present system—6 per cent of dust was obtained. The dust chamber is emptied every eight to fifteen days, according as the work is by day or both by day and by night. The blocks of basic slag are first broken up by hand to eliminate pieces of iron, which are laid on one side to return to the foundry. The basic slag so obtained is then reduced to a fine powder (passing through a 100 sieve) in ball mills. The powder is collected in the lower part of the mill and bagged up in 2 cwt. (220 lb.) bags. Formerly the basic slag was allowed to slake in the air, and the fragments after eliminating the iron were ground in flatstone mills. But basic slag slaked after long exposure to atmospheric agents sometimes contain excessively hard pieces, resisting the most forcible grinding; this method was abandoned. The treatment to which the basic slag is subjected as it comes from the convertor has a considerable effect on the grinding. V. Reis has examined the composition of basic slag and its concatenation with its resistance to grinding. From an outward inspection there are two kinds of basic slag, block slag and poured slag. Block basic slag is got when it is allowed to solidify in the wagons into which it is poured from the convertor. It then cools slowly and uniformly, and may be removed in a single block which is easily detached from the platform of the wagon. Poured basic slag is obtained by pouring the contents of the wagon on the ground. It spreads out in a thick layer and cools rapidly. This kind of basic slag is generally very hard; its grinding is difficult and requires a great expense of motive power. Basic slags in blocks, on the contrary, are more easily ground, but they also contain very hard lumps. The following table by Reis gives the composition of different slags and their resistance to grinding:—

TABLE LXI.—EFFECT OF COMPOSITION OF BASIC SLAG ON FACILITY OF GRINDING.[1]

	I.	II.	III.	IV.	V.	VI.	VII.
Silica . .	6·77	16·41	6·69	4·88	8·07	6·00	7·07
Phosphoric acid .	16·92	11·75	17·75	19·25	18·48	18·39	22·50
Alumina . .	1·68	1·58	0·95	0·59	1·40	1·37	0·89
Ferric oxide .	0·96	10·41	5·70	5·14	3·45	2·87	5·27
Ferrous oxide .	10·77	10·55	10·65	12·49	10·13	11·43	6·49
Lime . . .	51·00	31·00	48·42	48·17	46·47	50·77	47·36
Manganous oxide	7·16	14·91	7·71	6·23	9·35	7·28	7·81
Magnesia . .	3·01	2·08	2·05	2·38	2·03	1·57	1·67
Crushing . .	difficult	easy	easy	less easy	difficult	difficult	easy

I. Poured slag, dark brown, hard and difficult to grind.
II. Block slag, grey, lamellar, friable, easily ground.
III. Block slag, slate grey, firm, and easily ground.
IV. Block slag, grey, firm, vesicular, less easily ground.
V. Poured slag, dark brown, hard, brittle, difficult to grind.
VI. Block slag, brown, brittle, hard, difficult to grind.
VII. Block slag, grey, lumpy, difficult to grind.

It follows from these figures that in general the chemical composition of basic slag has only a slight effect on its physical properties, whilst the percentage of oxide of iron would appear to increase their resistance to grinding, as the following table shows:—

TABLE LXII.—SHOWING THE INFLUENCE OF THE RATIO OF THE PEROXIDE OF IRON TO PROTOXIDE ON THE EASE OF GRINDING OF BASIC SLAG.

Basic Slag.	Peroxide of Iron.	Protoxide of Iron.	Ratio of Fe_2O_3 to FeO.	Grinding.
1	0·96	10·77	1 : 11·2	Difficult
2	10·41	10·55	1 : 1·0	easy
3	5·70	10·65	1 : 1·9	,,
4	5·14	12·49	1 : 2·5	less easy
5	3·45	10·13	1 : 3·0	difficult
6	2·87	11·43	1 : 4·0	,,
7	5·27	6·49	1 : 1·2	easy

When the ratio of the peroxide of iron to the protoxide $< 1 : 3$ the basic slag is generally easily ground, especially when the peroxide of iron is in preponderant proportion, but when it is the protoxide of iron which predominates the slags are hard and difficult to grind. It is important to watch the sieves around the crusher, and see that they are working well, so as to be able to remedy any defect forthwith. With this end in view, the basic slag produced each time

[1] The translator has transposed the figures relating to lime and manganese.

by four crushers is carried to a weighing machine manipulated by a man of trust; the latter registers the production of each crusher, takes a small sample from each bag which he examines by the feel and the sieve and runs it into a box installed for the purpose, or each chief grinder weighs his product and is himself responsible for the good execution of his work and its bagging up. Then the sacks are carried to the depôt. As in the slack season orders must be executed from stock, it is necessary to use very sound and carefully sewn bags and to preserve them full in a dry place, because ground basic slag, owing to its high lime content, is apt to solidify in a damp place. The moistened powder cakes and cannot be rendered friable by ignition as one might suppose; it only becomes harder. The 2 cwt. bags (220 lb.) measure 50 × 90 cm. (say 20 × 36 in.). Even in using sound bags some of them rot when stored full. That is why basic slag is stored in iron silos.

It has already been mentioned that the cooling of basic slag is accelerated by quenching with water. This work is not without danger. When basic slag solid on the outside but incandescent inside is exposed to the shower of water, this may penetrate into the inside of the block by cracks and crevices; it is converted into steam which occupies a volume 1600 times greater at 0° C. and 7500 times greater at 1000° C. When such steam is given off instantaneously a very small quantity of water suffices to cause an explosion. It may also happen that a block of basic slag still liquid inside may have an escape, which is particularly dangerous for the workmen. It is necessary therefore to draw their attention thereto. Finally, gas may form inside the basic slag without exterior aid, which, in virtue of its tension, seeks a vent, and not finding any causes the block to fly away in pieces. When a crusher has to be repaired, and if the repairs cannot be done on the spot, it is conveyed to the forge on a rolling crane or on a truck running on rails. Crushing being a work which requires to be continuous, they are not stopped except for dinner at noon, otherwise they work continuously, the workmen replacing each other at lunch time. During the dinner hour the machines are inspected and the bearings lubricated. The grinding plant should be simple. Owing to the peculiar nature of the substance being ground, conveyors and mechanical feeders are not applicable. A crusher of 2 metres (6½ feet) can produce 15 tons in 10 hours of ground basic slag, when the basic slag is fresh cooled and not too hard. P. Mellman, of Berlin, German patent 107,234, projects a jet of steam or air into the liquid basic slag at the moment it is discharged by the convertor. The basic slag then becomes friable, and is very easily ground. The basic slag in blocks is sold to the grinding factories according to their percentage of phosphoric acid. The determination is generally made on the powder produced during crushing, supposing

that they possess covered and very dry warehouses. On the other hand, the vendor takes a sample from each block by chipping off a fragment with the hammer and takes a fair average sample at the end of each month. The sample is crushed, mixed, and divided into three parts; one part is sent to the buyer, the other to the sender, and the third is sealed and kept in reserve as a basis of settlement in case of difference. The exchange of analyses on both sides is made on a certain day, and the average is taken as a basis when the difference between the two analyses does not exceed 0·5 per cent P_2O_5. If the difference be greater, the sample in reserve is sent to an analytical station agreed on by both sides, and the analysis which it supplies forms the sole basis of adjustment. The cost of the analysis is borne by the party whose analytical results are furthest from those of the analytical station. If the analytical results on both sides differ to an equal extent from the experimental station, the costs of settlement are defrayed equally by both parties.

Basic slag is delivered to farmers without being mixed with other manures. If it be mixed with potash salts it heats and gradually solidifies; the caustic lime acting on the magnesium chloride forms magnesium oxychloride, which is a powerful cement; if mixed with sulphate of ammonia, the caustic lime acts on the ammoniacal nitrogen and causes loss. Finally, if mixed with nitrate, the nitric acid may be reduced into ammonia by iron, in the form of a fine powder, and the ammonia expelled by the caustic lime.

Customs in the Sale of Basic Slag.—From 1 July, 1895, according to a decision of the Assembly of German Agriculturists, basic slags were sold on the basis of their phosphoric acid soluble in citrate, without taking into account their total phosphoric acid, nor the degree of fineness.

But in its General Assembly held in 1898, the Union of Experimental Stations decided no longer to use Wagner's citrate of ammonia solution. It, moreover, found that steel works, to increase the solubility of their basic slag in citrate, were adding to the cast-iron not only silica, but more lime. The effect of this was to increase the alkaline nature of the basic slag, and the Union estimated that this increase in alkalinity justified the selection of a solvent of greater acidity in the estimation of soluble phosphoric acid. The 2 per cent solution of citric acid forms in fact a more accurate method than citrate of ammonia for basic slag prepared according to this new process. But Professor Wagner estimates that the 2 per cent citric acid solution dissolves 7 per cent of P_2O_5 more in basic slag, that is to say, it shows 16 per cent of soluble phosphoric acid where the old method only showed 15 per cent.

There is at the present time a tendency to value basic slag on the basis of its total phosphoric acid content, according to cultural experiments made on the subject by Meissl and Defert in Austria.

Remarks on the Use of Basic Slag.—It is not intended to examine here the use of basic slag on vegetation; that examination will find its place better in a special work just published by the author. The remarks made here will therefore be confined to a few points more immediately connected with the study of basic slag.

Guffroy, an agricultural engineer, having taken in hand researches as to what fertilizing action the silica and the manganese had in basic slag, isolated, as well as could be done, the blue crystals, silico-phosphate, and the brown crystals, tetraphosphate, examined above and caused them to be analyzed in Professor Grandeau's laboratory. The following are the results:—

TABLE LXIII.—ANALYSIS OF BLUE AND BROWN CRYSTALS IN BASIC SLAG.

	Brown Crystals. *Per cent.*	*Blue Crystals.* *Per cent.*
Total phosphoric acid . .	21·71	20·28
Lime	48·88	51·52
Silica	1·49	5·17
Manganese calculated to the metallic state . . .	2·46	1·86

Trials were made:—

1. With a basic slag of known composition.

2. With a basic slag presenting the same composition, and of which the phosphoric acid was furnished by crystals of tetraphosphate and silico-phosphate of natural basic slag.

3. With an artificial basic slag, where by using at one time only tetraphosphate, at another time silico-phosphate, there was got:—

(*a*) A basic slag deprived of silica.

(*b*) A basic slag containing little manganese.

From the comparison of the results obtained it was easy, consequently, to infer the action of the ingredients, manganese and silica. The first researches were made in collaboration by Guffroy, Milon, and Crepeaux. They have been summarized by the National Society of Agriculture.[1]

The plants experimented on were buckwheat, wheat, and violet trefoil. From this first series of experiments there is deduced the double efficacy of manganese and silica, in basic slag *Etoile* brand. The second series of experiments, the results of which are not published, were made by Guffroy and Milon alone, on wheat, buckwheat, and hemp; at the same time the violet trefoil of the first

[1] "Bullet. de la Soc. National d'Agric., 1905," pp. 479-83: "On the Fertilizing Action of Certain Accessory Products in Basic Slag".

experiment was kept under observation. The result of these experiments may be summarized thus :—

1. Apart from its phosphoric acid, lime and magnesia, *Etoile* basic slag has proved efficacious by its manganese and silica.

2. Manganese from an agricultural point of view ought to be regarded as an important constituent, influencing both the quantity and the quality.

3. It seems that silica, at least in the condition under which it exists in *Etoile* basic slag, also acts in the same direction, but that its action is weaker, less decided, and requires to be further studied to be established in a general way.

CHAPTER XII.

NITROGENOUS MANURES.

The most widely distributed nitrogenous manures are nitrate of soda (Chili saltpetre) and sulphate of ammonia. A third class of purely nitrogenous manures is that represented by animal waste. These (latter) products are of considerable agricultural importance, although the manure trade does not seem to take them sufficiently into account. These three forms of nitrogenized manures are not only differentiated by their chemical composition, but by their mode of action in the soil. They form therefore three distinct classes, which will now be examined.

Nitrate of Soda.—Nitric acid compounds have been known for a long period. It is probable, according to Herapath, that the ancient Egyptians used nitrate of silver to make their inscriptions on the bands in which they wrapped their dead; it is the same chemical compound as that known as infernal stone, which is used to mark linen and the skin. So far back as the eighth century of the Christian era, Geber and Marcus described a body which they called *salpetræ*, which corresponds with saltpetre, with nitrate of soda. In the twelfth century, Raymond Lulle called this body *salnitri*. Since then the term *saltpetre* has been used to designate nitrate of potash, whilst nitrate of soda is called Chili saltpetre, or nitre, in Great Britain.

Nitric Acid consists of nitrogen, oxygen, and hydrogen; its chemical formula is HNO_3. It thus contains fourteen parts of nitrogen (22·2 per cent), forty-eight parts of oxygen (76·19 per cent), and one part of hydrogen (1·59 per cent). It forms a very caustic fuming liquid (attacking organic matter, strongly burning the skin). In the concentrated state it has a density of 1·52 (104° Tw.), but the commercial acid is generally much weaker: D = 1·20 to 1·4 (40° to 80° Tw.). It decomposes easily. It gives up a portion of its oxygen to oxidizable bodies, such as carbon, sulphur, sulphurous acid, and then passes to less highly oxidized states. Metallic zinc reduces dilute nitric acid, and converts it into nitrate of ammonia. With bases it forms salts, which with the exception of some basic metallic salts, are soluble in water. Nitric acid is formed almost exclusively by the oxidation of ammonia, or of nitrogenous matter of animal origin, under the action of the air in presence of

bases (carbonate of lime). However, this spontaneous formation in the soil is very slow in our climate. It is, on the other hand, very rapid in Southern countries, Bengal, Hungary, Spain, where the conditions of temperature and of moisture in the air conduce considerably to the oxidation of nitrogenous animal matter.

For a long time these countries where nitrates exude spontaneously from the soil, and cover it with a layer like hoar frost, alone supplied Northern Europe, up to the time when they succeeded in making mixtures of soil to produce saltpetre. This industry was conducted in saltpetre fields. Limestone, marl, washed wood ashes were mixed with animal matter, urine, dung, straw, etc. Heaps were made, which were left to themselves in the open air for nearly a year, frequently turning them. When the earth was ready, that is to say enriched, it was lixiviated. To eliminate the lime from the liquor obtained, it was treated with wood ashes, and clarified, and evaporated to obtain saltpetre. That method, which requires much work and only gives poor results, could only be applied in countries which, deprived from communication with the south, as in time of war, were obliged to live on their own resources, as France and Germany were during the continental *blocus*. This method, therefore, was abandoned.

But the sources of saltpetre indicated above barely met the wants of industry; agriculture could not profit. The discovery of an important deposit of nitrate of soda in America, the working of which was commenced in the years 1825-28, enabled the wants of agriculture to be met.

Chili Nitrate of Soda.—South American nitrate of soda is distinguished, more especially from ordinary saltpetre, by the fact that its acid is combined with another alkali. In Indian saltpetre it is combined with potash (KNO_3), whilst in Chili saltpetre it is combined with soda ($NaNO_3$). It is met with in the Pampas of Peru, of Chili, and Bolivia, between 19° and 27° of south latitude; it abounds especially in the province of Tarapaca (formerly Peruvian, now Chilian) and in the desert of Atacama. The nitrous mineral caliche, or *terra salitrosa*, occurs as a layer of 1 to 6 inches thick under a bed of conglomerate, consisting of sand, feldspar and pebbles, amalgamated by a cement consisting of clay and different salts forming a bed 20 to 30 inches thick. Its colour varies from grey to brown. The conglomerate bed is sometimes awanting, so that the mineral crops out at the surface.

The *caliche* is never pure nitrate of soda. It contains mixtures of nitrate of potash, common salt, iodide and bromide of sodium, alkaline sulphates, sulphate of lime mixed with sand. It only contains on an average 25 per cent of nitrate. Picked pieces contain more. The following gives the percentage in nitrate of different products :—

TABLE LXIV.—SHOWING COMPOSITION OF CALICHE.

	Saltpetre. *Per cent.*	*Common Salt.* *Per cent.*
Yellow salt, pure hard, with small crystals . .	77·9	12·9
Yellow salt, pure porous soft, with large crystals .	65·7	28·12
Yellow caliche, veined with brown . . .	64·73	32·02
White caliche, hard and with small crystals .	60·50	14·30
White caliche, porous and large crystals . .	68·03	28·12
Brown caliche, porous and large crystals . .	36·80	20·70

Opinions differ as to the method of formation of this deposit, which occupies a surface of about 60,000 hectares (say 150,000 acres) and contains about 170,000,000 tons. Hilliger's is the most likely theory; he believes that the nitrate is formed from the nitrogen of guano deposits, which covered the shores of a great soda water lake by a process analogous to that to be seen in Hungary in our own time. The soda salts of the sea water would simply convert the saltpetre into nitrate of soda. This opinion has in its favour all the facts and circumstances met with in the deposit. Moreover, traces of guano are still found in the crude salts. To extract the crude salt a hole is dug in the ground 50 cm. (20 in.) in diameter; when the saltpetre bed is reached a chamber 90 to 100 cm. (35 to 40 in.) in diameter by 30 cm. (say 12 in.) deep, and 150 to 200 kg. (3 to 4 cwt.) of powder inserted. By exploding the powder by means of a fusee, a considerable surface of the deposit is laid bare often on a radius 10 metres (say 40 ft.) from the hole. The crude salt is hand picked, to eliminate stones and fragments of less value; it is charged into baskets or into trucks, which camels transport or draw to the melting workshop. To dissolve the crude caliche three kinds of apparatus are used, viz. :—

1. *Open Cast-iron Pans—Paradas.*—These are heated by naked fires. Two pans 2 metres in diameter (6 ft. 6 in.) are used for one furnace. Well water or water from a previous operation is run in, then it is charged with caliche or crude saltpetre reduced to pieces the size of the fist. When the solution is concentrated enough, it is run into cases or boxes, where it clarifies; it is then decanted on the top of the depôt and run into iron or wooden crystallizers; 40 per cent of crystals is thus obtained and 60 per cent of mother liquor.

2. *Cylindrical Vertical Pans—Maquinas.*—These are heated by direct injection of steam. They are 8 to 10 metres (26 to 33 ft.), with a diameter of 4 to 5 metres (13 to 16 ft.). Each of these pans yields in twenty-four hours 46 to 148 tons of saltpetre. The clarified solution is poured into wrought-iron crystallizers 4 to 5 metres (say 13 to 16 ft.) square and 0·5 metre (say 20 in.) deep; crystallization lasts three to four days. The steam given off contains an important amount of iodine which can be avoided by an addition of soda.

3. *Vessels heated by a closed tubular bundle (? steam coil)* which have been introduced by the British and German companies. These vessels measure 11 metres (36 feet), 1·85 metre (6 ft.) wide by 1·85 metre (6 ft.) high, into which the mother liquor and the wash water are run and heated to boiling, then six trucks of perforated wrought-iron containing about 4 tons of caliche. The nitrate dissolves in the water whilst the residue remains in the trucks. To hasten solution the liquid is agitated by injection of steam and of hot air under each truck by means of a Koerting's injector. This plant works more economically than the preceding. At the same time the solutions so obtained are more pure and more concentrated. To get a ton of nitrate requires 3 tons of caliche. The crystallized nitrate is left to drain, then it is dried in the open air. Nevertheless it always remains slightly moist owing to the presence of chlorides of calcium, of magnesium, and possibly also of nitrates of calcium and magnesium. It crystallizes in rhombohedra, and has a dirty reddish-grey appearance, due to its oxide of iron content and to bituminous substances. The residue left by the solution (*ripio*) still contains from 15 to 35 per cent of $NaNO_3$. It is boiled with water and a weak solution of 43 to 45° B. obtained, which is utilized to dissolve a fresh charge of crude salt. The muds from the clarification are treated in the same way. According to Dr. Langbein, they contain 67·1 of common salt and 27·3 of nitrate of soda.

Chilian nitrate of soda, such as dispatched from the spot of production, has the following composition :—

TABLE LXV.—ANALYSIS OF CHILIAN NITRATE OF SODA.

	Per cent.	*Per cent.*
Nitrate of soda	94·0	15·31 N.
Common salt	1·52	
Potassium chloride	0·64	
Sodium sulphate	0·92	
Sodium iodide	0·29	
Magnesium chloride	0·93	
Water	1·36	
Boric acid	traces	
	99·60	

Better equipped factories supply nitrate of the following average composition :—

TABLE LXVI.—ANALYSIS OF BETTER QUALITY NITRATE OF SODA.

	Per cent.
Nitrate of soda	96·00
Common salt	1·00
Soluble sulphate of soda	0·50
Insoluble	0·25
Water	2·25
	100·00

Common salt and soluble sulphates may be eliminated by washing with cold water and by centrifuging. The content in nitrate is evidently not always constant; it generally varies between 90 and 100 per cent, which corresponds to a strength in anhydrous nitric acid of 57·2 to 63·5 or of 14·8 to 16·4 per cent of nitrogen. In Great Britain the fraction which goes to make up 100 per cent is regarded as refraction, so that a nitrate of 5° of refraction means a nitrate of 95 per cent strength. This remark is important, so as to understand market reports. On different occasions chlorate and perchlorate of potash have been found in nitrates. Now these substances are liable to spontaneous combustion, besides they are injurious to vegetation. The presence of perchlorate is attributed to the negligence of the workmen who have omitted to cool the solution of caliche in the pan and have set it aside to crystallize in the hot state. This perchlorate may be extracted from the substance by the method which was the subject of German patent No. 125,206. But since the disastrous effect of perchlorate on vegetation has been recognized and the nitrates which contain it refused, manufacturers have been more careful, and perchlorate is now only rarely met with in nitrate.

One hundred parts of water dissolve of nitrate of soda at

0°	10°	20°	30°	40°	100°	121°	Boiling-point of the solution.
71	78	88	98	109	178	224·8	Parts.

The specific gravity of nitrate of soda is 2·244.

Nitrate of Potash.—A compound of nitric acid with potash has no interest but for industry; it is too dear to be used in agriculture, for up to now it is only made from Chili saltpetre and potassium chloride. It forms in itself an excellent manure, seeing that it contains not only nitrogen but also potash in a very pure form. Lately, however, important deposits of nitrate of potash have been discovered in South Africa, especially in the neighbourhood of Mabelstadt, and of Peliska in Cape Colony. But these deposits do not appear to be exploited.

Before terminating this subject, mention may be made of a nitrogenous manure put on the market in 1874, which has given good results. It is a double nitrate of potash and soda; it contains in 100 parts, according to Maercker:—

TABLE LXVII.—ANALYSIS OF A DOUBLE NITRATE OF POTASH AND SODA.

	I. Per cent.	II. Per cent.	III. Per cent.
Nitrate of potash	34·18	41·78	11·51
Nitrate of soda	62·22	55·27	82·94
Common salt	2·67	0·57	3·43
Water	0·46	1·67	2·02
Therefore—			
Potash	15·92	19·47	5·31
Nitrogen	14·89	15·05	15·24

Storing and Handling of Nitrate.—Nitrate of soda is marketed in the original sacks (catch-weight) weighing 120 to 140 kg. (264 to 308 lb.). It forms a mixture of crystals of different sizes. It also draws moisture from the air; when it is preserved in sacks they rot after some time and tear with the slightest pull. When the sacks are emptied, one part of the material, always moist, remains adherent to the fabric, from which there results not only a loss of matter, as also a loss of sacks, as these gunny bags then become unutilizable and are liable to catch fire.

Nitrate of soda is often coloured yellow by the presence of chromate of potash or violet by the presence of nitrate of manganese. The presence of nitrate of potash or of magnesium chloride renders it deliquescent; hence arises loss by the drainage of dissolved nitrate; that is why the bags are lodged on beds of plaster or clay which absorb the liquid. But it is best to spread the nitrate intended for mixing in not too warm a place. The bags are washed with tepid water, and the solution is added in the manufacture of superphosphate which has to be mixed with nitrate,[1] or it is concentrated in a pan. Certain manufacturers content themselves with beating the bags free from the adherent salt. If the nitrate ought to be employed alone it is screened and the lumps crushed in a Carr's disintegrator, or in the toothed roll crusher. It is dried in the old phosphate drier. However, if it be stored for a certain time in a place that is not heated, it gradually becomes moist. In consequence of the risk of fire, the building in which nitrate is stored should be isolated and built entirely of iron.[2]

Production of Nitrate in 1907.—The exports authorized by the syndicate of nitrate of soda manufacturers of Chili, rose to 2,050,000 tons for the year 1 April, 1907, to 31 March, 1908. Of these quantities 1,750,000 tons had to be delivered before the end of the year 1907, and the remainder, say 300,000 tons, in the months of January, February and March, 1908. Now these exports made from April to December, 1907, only amounted to 1,225,000 tons. The cause of this decrease lies in the first instance in the labour crisis. The Chilian labourer more fit than any other to work under the torrid sun of the Pampas, is as improvident as he can be. He only works when he must do so to live, and as wages are very high in nitrate

[1] This nitrate liquor if used up in wet mixing of manures might aid drying, but it would all be converted into sulphate of soda. If poured on to a finished superphosphate it would convert it into a wet paste, and after spoiling the manure no credit would be given by the analyst for the nitrogen.—Tr.

[2] If sulphuric acid be made in the manure works, as is often the case, the amount of nitre required for the pyrites burners should be fetched daily from the store referred to in the text. The supports of the chambers are of pitch pine, and if nitre bags full or empty heat in the neighbourhood of the kilns or chambers the latter run the risk of being completely burnt down. Storing nitre in the original bags is bad management. They are far too heavy and clumsy to be lugged about by one man.—Tr.

factories he only works a few days, and then rests under such conditions; the factories work very irregularly. The present prices are about 10s. 10d. a cwt. The rise in the price of nitrate which had been discounted by the syndicate of manufacturers will always be limited by competition with sulphate of ammonia. The latter, in fact, after experiments made by Kraus at Weihenstephan, should produce the same effect as nitrate, with this difference that it acts more slowly.

Ammoniacal Salts.—Ammonia is a compound of nitrogen and hydrogen, according to the formula NH_3, and forms a decomposition product of nitrogenized organic matter. It is a gaseous body, giving off a characteristic pungent odour. It is very soluble in water. The solution is generally known as ammonia. It has an alkaline reaction, and turns red litmus paper blue. Under the influence of the oxygen of the air, ammonia is partially converted into nitric acid. It forms salts with acids, by combining with these acids to form a metallic radical NH_4 which is ammonium. Thus sulphate of ammonia is formed according to the equation :—

$$H_2SO_4 + 2NH_3 = (NH_4)_2SO_4$$

and ammonium chloride according to the equation :—

$$HCl + NH_3 = NH_4Cl.$$

All ammoniacal salts give off ammonia when they are placed in contact with alkalies or caustic lime. Ammoniacal compounds are very widely distributed in nature, but always in small quantities. Their presence has been determined in the air and in rain water, also in the juice of almost all plants. Ammonium chloride is found in salt springs, in volcanic emanations; carbonate of ammonia in large quantities in the guano deposits of Peru, Bolivia, and Chili, and the western part of Patagonia. The principal sources of ammonia for industry and for agriculture are certain substances of animal origin (bone, meat, blood) or vegetable (coal, peat), which, submitted to dry distillation, give off the greater part of their nitrogen as ammoniacal compounds.

Ammonia is, likewise, obtained by the distillation of fæcal matters in presence of caustic lime and by the treatment of gas (wash) liquor. Left to stand, urine putrefies; the urea is transformed into ammonia, which treated by caustic lime yields ammonia and carbonate of lime. Ammonia is also found in the smoke of factory chimneys and in coal soot; the latter may even sometimes be utilized as a manure, as the following analysis by Hutton of Glasgow of coal soot shows :—

	Per cent.
Potash	0·30
Phosphate of lime	3·20
Ammonia	2·80
Equal to nitrogen	2·30

Formerly, ammoniacal salts were made solely from matters of animal origin. They were charged into retorts which were heated to incandescence, the vapours given off being condensed. The carbonate of ammonia thus obtained was collected and purified or combined with acids to form different salts. The process is still applied in the manufacture of small quantities of sal-ammoniac, but solely as a bye-product in the manufacture of animal charcoal. The calcination of the bones is done after two different methods. The one, the older, consists in charging the raw material in vessels placed in a furnace in stages so that one serves as a lid to the other underneath. The vapours given off during combustion, the details of which need not be dwelt upon, escape outwards by the chimney. The other method consists in calcining the bones in a cast-iron retort analogous to that used in distilling coal. The gases which are given off are collected and condensed. The products of the condensation contain among other useful substances ammonia, which can be extracted by distillation and converted into sulphate of ammonia. But, as already observed, bone black is no longer used in sugar factories. With the disappearance of bone black, the bye-products, especially ammonia, also disappeared. The most important source of ammonia is at present coal, the percentage of nitrogen in which varies from 0·5 to 1·6 per cent. The extraction of ammonia will therefore be studied in the following order: (1) In the manufacture of gas; (2) in the manufacture of coke; (3) in the blast furnaces, and (4) in the gasogene ovens (Mond's process, Bourgeois and Lencauchez' process).

Manufacture of Sulphate of Ammonia by Distillation of Gas Liquor.—When coal is distilled, the nitrogen which it contains passes partly into the tar as complex products (aniline and its analogues) and partially in the form of ammonia in the illuminating gas. The ammonia is eliminated from the latter by washing with water. According to Roscoe, only 14·5 per cent of its nitrogen is obtained from coal as NH_3, 35·26 per cent is lost as free N, whilst the coke retains 48 to 68 per cent. This low yield of ammonia is due to the facility with which this gas is decomposed (at a temperature of 500° C., Ramsay and Young). This loss may be avoided by preventing the gas in the retort from coming in contact with the heated sides. According to Beilby, this desired result is obtained by distilling coal with steam. By this method as much as 50 to 56 kg., say 110 to 123·2 lbs., of sulphate of ammonia per ton of coal may be obtained. Gas liquor consists in reality of a weak solution of ammonia, carbonate of ammonia, sulphide of ammonia, cyanide of ammonia, and sulphate of ammonia. Its nitrogen content varies considerably, as the following analysis by Arnold, in 1889, shows:—

TABLE LXVIII.—ANALYSIS OF GAS LIQUOR FROM COALS OF DIFFERENT ORIGIN.

One litre of gas liquor contains the following ingredients in grammes, or 100 gallons contains in lbs.	Gas Liquor from the Coal of				
	Zwickau.	Zwickau.	La Rhur.	La Saare.	La Saare.
Total ammonia	12·09	9·40	18·12	15·23	3·47
Hyposulphite of ammonia	1·036	1·628	5·032	2·072	6·296
Sulphide of ammonia	6·340	0·646	6·222	2·468	1·428
Bicarbonate of ammonia	1·050	1·470	2·450	33·763	5·856
Carbonate of ammonia	4·560	7·680	33·120		
Sulphate of ammonia	0·462	0·858	1·320	4·922	1·926
Ammonium chloride	30·495	17·120	3·745		

According to the same author, the ammoniacal liquor from a British gas works contained in grammes per litre (lbs. per 100 gallons) :—

TABLE LXIX.—ANALYSIS OF BRITISH GAS LIQUOR.

	lbs. per 100 *gallons.*
Ammonia	20·45
Sulphur total	3·92
Ammonium sulphide NH_4H_5	3·03
Ammonium carbonate $(NH_4)_2CO_3$	39·16
Ammonium chloride	14·23
Rhodanate of ammonia	1·80
Sulphate of ammonia	0·19
Hyposulphite of ammonia	2·80
Ammonium ferrocyanide	0·41

It will be seen from these analyses that carbonate of ammonia preponderates; its percentage of ammonia chloride is likewise high.

Production of Ammonia in the Manufacture of Coke.—If in the very beginning of illumination by coal gas steps were taken to collect the ammonia produced in the purifying of gas delivered for consumption, it was not so in the manufacture of coke, where this body was for a long time totally rejected. The coke industry, as it is now conducted, yields products identical with gas. The first attempts at recovery of the ammonia were made by Stauf in 1764 in a Saarbruck foundry. But it was not until 1858 that Charles Knab constructed at St. Denis the first plant that gave good results, introduced by Carvès at Commentry in 1762. It was erected in 1866 at the Besseges Forge, then in 1879 at *Terre Noire*. In 1882, Simon of Manchester improved the Carvès coke oven by recuperating the heat to reheat the air to 500° C. or 600° C. The shape of these ovens was completely altered. Knab's ovens, wide and flat, heated under the sole only, and carbonizing at a low temperature, have been completely abandoned to give place to Carvs,

Simon-Carvès, Otto and Semet-Solvay ovens, high, narrow, long, carbonizing rapidly and at a high temperature. The furnaces actually in use may be divided into two classes :—

1. Those which are only a modification of the ordinary coke oven, where the heating is effected by the admission of air into the interior, and burning a part of their carbon as fuel (Jameson, Aitken, Luhrmann types).

2. Those in which air is not admitted into the interior, the heat being applied on the outside by the combustion of the gas which escapes during distillation, and after separation of tar and ammonia. Almost all modern coke ovens belong to this class (Hoffmann Otto, Simon-Carvès, Bauer, Hussener, Semet-Solvay, etc., types). Here, in a few words, is the general principle followed in coke ovens of the present day. All are built, apart from numerous details, in such a manner as to have a hermetically sealed chamber, from which the gas distilled from the coal is aspirated mechanically without admission of air. The gas afterwards passes through condensers, cooled on the outside by air or water, where they deposit the greater part of the ammonia and the tar; the small remaining portions are decomposed in the scrubbers (coke columns). The residual gas is then led to the *tuyeres* which heat the retorts, and inflamed by means of a current of hot air issuing from the recuperators. After having accomplished this heating, the residual gases pass into the heat recuperators. Certain German coals yield 11·5 kg. (25·3 lbs.) of sulphate of ammonia. By the Semet-Solvay ovens, as much as 7 to 17 kg., say 15 to 37·4 lbs., of sulphate of ammonia per ton of coal distilled are obtained.

The working of these ovens is regulated by various conditions. The coal introduced into the oven ought, to give a good coke, to be instantaneously submitted to a very high temperature, and the calcination ought to be conducted rapidly and without stoppage. That is why the heat is transmitted by as thin ovens as possible, as in the Semet-Solvay oven. In the Hoffmann Otto oven the gas given off by distillation escapes through two orifices in the arch of the oven and passes into gas reservoirs placed above and across the ovens; then it is lifted by aspirators, and drawn through pipes to condensers and washers, in which the tar and ammonia is deposited. Freed from these two substances the gas is brought back through another pipe, under the sole of the ovens. The inflamed gas follows alternatively vertical flues, ascending one half of the flues and descending the others. In the Semet-Solvay system the flues in which the gas burns, and which generally are fitted into the main flue, are here independent, and consist of retorts with their encased sides the one in the other, and forming a complete and tight circuit.[1]

[1] The Hoffmann Otto is 10 metres (say 40 feet) long, 0·4 to 0·6 metres (say 16 to 24 inches) wide, by 1·70 metres (say 5 feet 8 inches) high. The Semet-Solvay

The Carvès, the Tamaris, the Terre Noire, and Bessege ovens, producing together about 300 tons of coke per day, yield 6 tons of tar and 2 to 2·5 tons of sulphate of ammonia.

The advantages of recuperation become more and more evident, and in spite of the expense which the installation of such plant involves, many mine proprietors have not hesitated to build similar ovens.

The working of a battery of four coke ovens entails a supplementary staff to work the gas-extractor, and to keep in order and clean the recuperation appliances. The cost of the Semet-Solvay furnace, refractory masonry with lining, oven discharger, discharger flue, water piping, etc., is £240 sterling. The extractor, pump, and recuperation appliances cost £140 sterling. Each oven takes 5 tons of coke; the operation lasts about twenty-four hours. The Hoffmann Otto takes a charge of 5 to 6 tons. The use of these ovens has extended very rapidly in France; there are at present several hundreds of them. The Hoffmann Otto are almost exclusively used in Germany and Austria. The Semet-Solvay are used in Belgium, in France, Great Britain, Germany and the United States.

Recovery of Ammonia from Blast Furnaces.—The recovery of the ammonia contained in the gas from blast furnaces is only carried out in Scotland at Gartsherrie. The coal used is a non-caking coal, which prevents previous conversion into coke. The gases escaping from the furnace mouth pass through a series of pipes into apparatus similar to those used in the gas manufacture, followed by a series of scrubbers, fitted with perforated plates, leaving the gas to pass alternatively on each side, whilst a thin stream of water, constantly flowing, dissolves the entrained ammonia. The liquid is repumped and sent back to the scrubbers, until sufficiently saturated. The yields are on an average 0·9 to 1·36 of the weight of the coal, which corresponds very nearly with the amount of ammonia got by the Carvès coke ovens.

Recovery of Ammonia formed in Gas Producers.—Heating by the gas obtained in the semi-distillation of coal is one of the best processes now known. It suppresses various drawbacks incidental to a great number of fires, and enables very high temperatures to be obtained. In this distillation, as in all similar treatment of coal, there is given off at the same time as the combustible gases a rather important amount of ammonia. To give good results the production of the gas is effected by alternating the two following operations:—

1. The vapour of superheated steam is directed on to coal, heated

is 9 metres (say 30 feet) in length, by 1·70 metres (say 5 feet 8 inches) high, and of a width, varying according to the quality of the coals to be treated, of 0·36 to 0·42 metres (say 14 to 17 inches). The air is heated to 200° to 300° C. (392° to 572° F.).

to redness, which lowers the temperature, owing to the heat absorbed by the decomposition of water.

2. The combustion is stimulated by a current of air to bring the temperature to its initial point.

The gas produced in this second phase very much resembles gas from a gas generator, called Siemens' gas. The mixture of air and steam is suitably adjusted. Amongst the gasogene plant constructed on this principle mention may be made of Siemens', Schilling's, Powson's, Wilson's and Mond's.

1. *Mond's Process.*—Mond was the first to inaugurate in England this new process of extracting ammonia from the products of combustion of coal itself. Coal is burnt in the gas generator in a mixture of air and steam, in such proportions that there are two tons of steam per ton of coal distilled. The temperature of the combustion is lowered to about 500° C. (932° F.). This excess of steam favours the production of ammonia; the third only of the steam which passes through the gasogene is decomposed. The gas producers are rectangular in form and arranged in series. They are 1·82 metres in depth and 3·65 metres long. The ash pits fitted with a hydraulic joint capable of resisting 0·10 metre water pressure. The air arrives above the level of the ash pit. The gas escapes from the centre of the top of the gas producer.

The gas which escapes from the gas producer traverses a washer with blades, Standard type, in which the ammoniacal salts are dissolved. Then at a temperature of 100° C. it passes into the first scrubber, drenched with a 38 per cent solution of sulphate of ammonia to which a known amount of sulphuric acid has been added.

The gas contained at its entrance into the scrubber 0·13 per cent of ammonia by volume, it now only contains 0·013 when it issues at a temperature of 80° C. It then enters the condenser containing wooden baffles pierced with holes, where they meet a current of water which is heated to 78° to 80° C. (172·4° to 176° F.) in condensing the steam. The gas, purified and cooled, passes to the burners. The hot water obtained passes to a third scrubber, into which a current of cold air is passed, which it saturates with moisture, and which brings the temperature to 76° (168·8° F.). That air is then forced into the gas producer. The yields obtained have been 32 kg. (70·4 lb.) of sulphate of ammonia per ton of coal, which is a beautiful result.

Attempts have been made to produce ammonium chloride direct by introducing hydrochloric acid gas into the furnace or by mixing the fuel with clay impregnated by calcium chloride. The results were not satisfactory.

Hennin proposes to operate like Mond, but by using high pressure steam slightly superheated and suitably diffused in the mass of the fuel, in the proportion of 0·75 to 1 per ton of coal.

2. *Bourgeois and Lencauchez' Process.*—Bourgeois and Lencauchez have patented a process the object of which is to collect the tar and ammonia in the gas distilled from coal, this operation not diminishing the calorific intensity of the gas. The plant which they propose to use therefore appeals to all industries, glass works, metallurgical industries, etc., which instead of burning coal under ovens, begins by converting it into gas in any kind of gas producer. It consists of three main columns. The first, cooling and washing the gases, is intended to retain tar and oils, which are collected in a lower cistern. In the second, the gas charged with ammonia meets a shower of acidulated water. The third is intended to stop the last traces of ammonia and to convey them into the first, and so on. From the preceding it will be seen that those industries which formerly did not utilize in any way the nitrogen contained in their fuel, are going to become one of the most important sources of ammonia.

Manufacturing Plant.—In the various ammonia-producing industries which have just occupied our attention, the manufacturing plant consists, above all, of condensers and distilling columns.

Condensers.—The condensers are generally refrigerators, the extractor, the washing condenser of some kind of system, and the scrubbers, or coke columns. Refrigerators are used in the manufacture of gas. The issuing gas is aspirated by the extractor, which is nothing but a suction and pressure pump. There exist a certain number of washing condensers. The following are mentioned: The Standard washer, the Chevalet washer, the Lunge Plate washer, the Pelouze and Audoin washer. The Standard washer consists of a series of cast-iron compartments, variable in number and dimensions according to the capacity of the plant. Each compartment contains a certain number of wrought-iron discs bolted together and locked on the shaft. These discs of thin sheet-iron, 2 to 3 mm. ($\frac{1}{12}$ to $\frac{1}{8}$ inch), thus present an enormous absorption surface. The latter traverses the washer in an opposite direction to the gas: the discs half dip into the water. An improvement has been made by replacing the sheets of iron by pieces of wood, cut in the form of a prism and arranged in quincunxes. This apparatus is almost exclusively used in Great Britain. The washers restore to the scrubbers their true rôle, which is to arrest the last traces of ammonia. The filling of the scrubbers varies much; sometimes washed coke is used, sometimes wood shavings, fragments of pumice stones, or of perforated bricks. The lining ought to be done carefully, for on it greatly depends the amount of water to be introduced. A driblet of water, well spread over well-arranged materials, will give as good an exhaustion as enormous quantities of water over a bad lining. The water escaping from the scrubbers should be carefully controlled. The

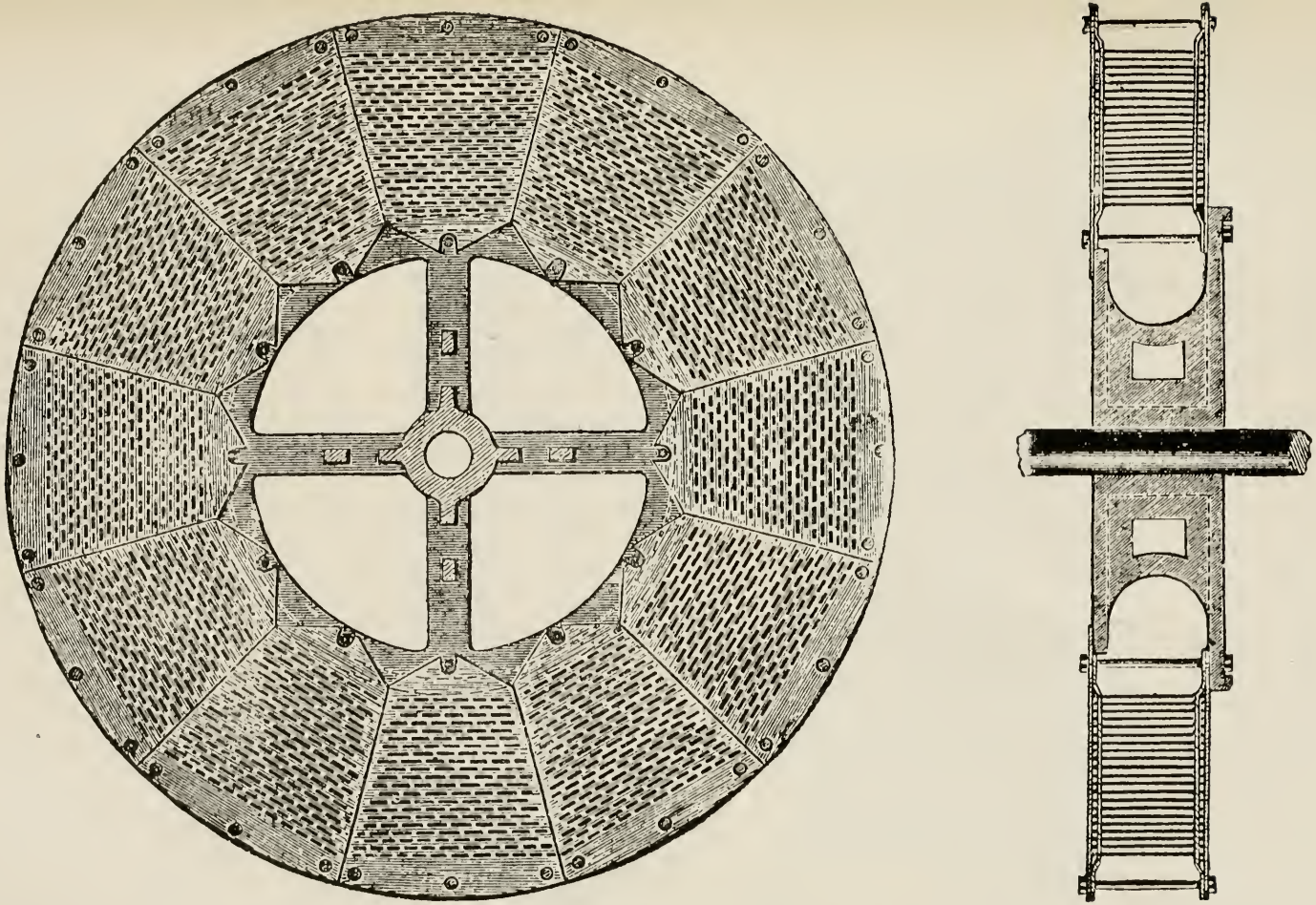


FIG. 38.—Plan and Section of Wooden Discs of the Standard Washer.—The disc is mounted on a central vertical shaft, from which radiate four bosses, supporting the part in the form of a crown, which is the essential organ of the apparatus. This crown is bounded above and below by wooden plates, in the intervening space of which there is arranged a multitude of small wooden prisms; the extremity of these is seen in the left-hand figure, and they are seen at full length in the right-hand section. They are rods which, dipped in the water at each turn of the disc, present a considerable absorption surface for the ammoniacal gas which comes in contact with them.

density of the ammoniacal water ought to be taken, and it must be seen that the escaping gas contains no trace of ammonia.

Chevalet constructed a scrubber of wrought-iron or of cast-iron, containing cast-iron vessels 8 inches apart and pierced with a great number of holes, carrying a chimney a little less in height than the

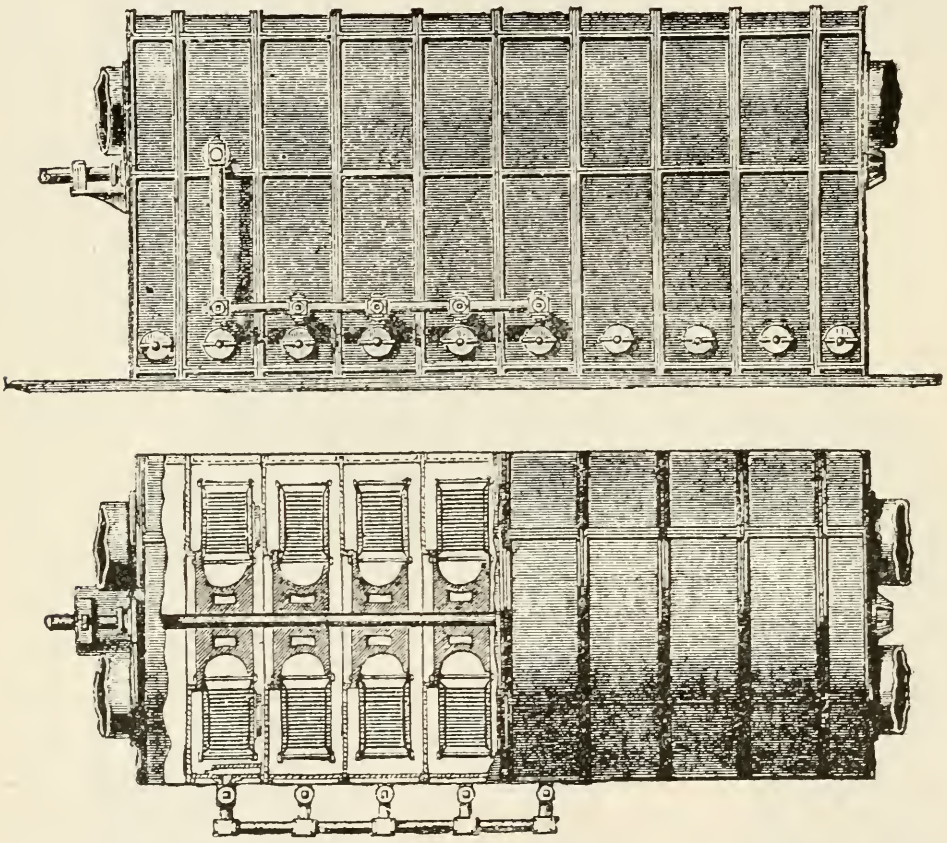


Fig. 39.—Standard Washer furnished with its different Discs.—The upper figure shows the outside appearance of the face of the washer; in the lower figure the washer is seen from above; the top side has been partly removed to show the interior arrangement. The discs of Fig. 38 are shown mounted side by side on the same shaft; their lower part dips in the water when the shaft turns; the moistened discs come in contact with the gas which passes to the upper part. This latter is dissolved. A peculiar system of partitions forces the gas to enter into intimate contact with the rods of the discs and to dissolve almost completely.

edge of the vessels. Each vessel is fixed in a ring without bottom of the distilling column. Between each vessel wooden shavings or coke is packed.

Distilling Plant.—All methods used to manufacture sulphate of ammonia consist essentially in disengaging ammonia from its salts, in submitting it to distillation, in conducting the ammoniacal

vapours into a receiver containing sulphuric acid, and evaporating the solution obtained, so as to extract from it the sulphate of ammonia by crystallization. The ammoniacal salts are decomposed by lime which is added to the gas liquor before distillation. In old distilling plant, working by naked fire, the use of lime required precautions, because it was liable to adhere to the bottom of the boilers; in modern plant heated by steam this drawback has disappeared. Sometimes the two methods are combined, that is to say, the gas liquor is first distilled such as it is, and then it is redistilled after adding lime. The latter is used either as quick-lime or as milk of lime, and in quantity varying with the content of the ammoniacal liquor. But the amount used never exceeds 5 per cent of the material. The distillate consists mostly of a mixture of water and free ammonia; organic bases—the most volatile—are also present along with tarry matter. As amongst all these bodies ammonia is the most volatile, the principle of hot or partial condensation has been applied to its distillation, a method which is especially important in the distillation of alcoholic liquids. In the older plant the distillate traversed one or more vessels containing reheated ammoniacal liquor. By this arrangement the ammonia was separated from the less volatile products which condensed on the road; on the other hand the ammoniacal liquor was brought to a high temperature before being distilled. However, this method cannot be adopted except by working continuously. The plant used in distilling ammonia may be divided into two classes, viz. (1) *naked fire stills* and (2) *steam stills*. Although less economical and of much smaller output, naked fire stills have still numerous advocates, because their installation is generally less costly and their management very simple. A few stills of both types will now be described.

Naked Fire Stills—The English Still.—An old still which is still in use in certain English factories where it gives excellent results is that shown in Fig. 40. It consists of a small boiler A, which is fed with gas liquor from a reservoir. If the liquor be heated to boiling, the free ammonia, and the carbonate of ammonia, the sulphide, and the cyanide of ammonium, all very volatile products, are given off with the steam, rise in the pipe *a*, pass into pipe *g*, whence they pass by the pipe *c* into the lead-lined wooden vat C containing concentrated sulphuric acid. The latter absorbs the gas and the vapours with effervescence, which renders them liable to return into the chamber A. To avoid this mishap a valve *h* is fitted to the top end of the pipe *c*, which opens from the outside to the inside and lets the air enter as soon as the acid begins to rise in *c*, i.e. as soon as the pressure in the apparatus is lower than the atmospheric pressure. When the operation is thought to be sufficiently far advanced, the test tap *d* is opened and the vapours coming from the boiler are tested with red litmus paper

to see if they still contain an important proportion of ammonia. If the test shows that the liquor is exhausted it is run into the boiler B, placed at a slightly lower level alongside the boiler A. With this end in view the boiler A communicates on the opposite side with the boiler B by a pipe *d* (Fig. 41), which is naturally at a level high enough not to be reached by the fire. It suffices to open the taps *e*, *f*, *i*, and *k*. Milk of lime is added in the boiler B to the water from A. The boiler A is recharged, and the taps *i* and *k* being closed, the contents of the two boilers are brought to the boil, whilst the same process goes on as already described in the boiler A; pure ammonia gas is formed in the boiler B as the result of the decomposition by the caustic lime of the chloride and sulphate of ammonia still contained in the water which had been treated in A. This gas also passes into the vat C; when a test at the test-tap

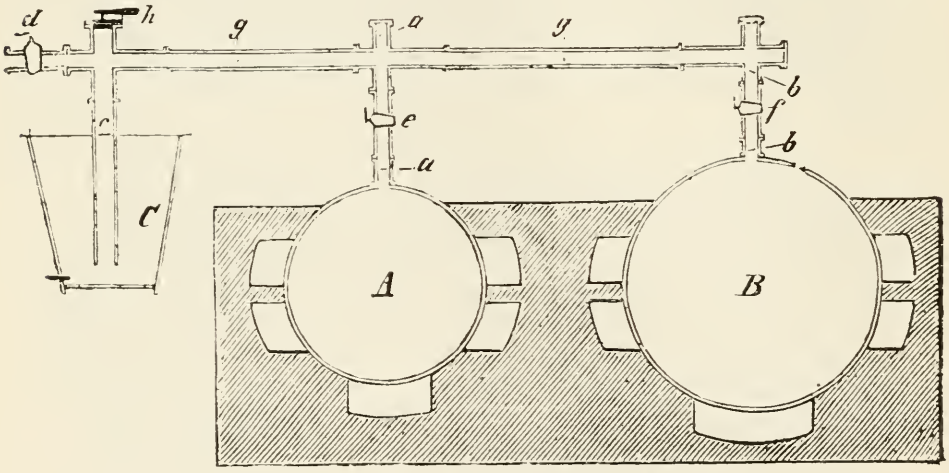


FIG. 40.—Naked Fire Ammonia Still.

shows that all the ammonia is volatilized, it is presumed that the water in the boiler B is exhausted and is run off. For that purpose the pipe *d* is fitted with two short pieces *m* and *l* closed with wooden plugs. To run off the liquid all that has to be done is to open them as well as the tap *k*. Ammonia can also be distilled in a single boiler, taking care to mix the milk of lime with the gas liquor beforehand. As the residual liquid would then contain not only chloride and sulphate of lime, but also carbonate of lime and various other salts, and as the mass of these insoluble salts would greatly hinder distillation, it is better to use two boilers, besides the sides of the boilers would become encrusted with lime salts and rapidly put it out of use. When the sulphuric acid in the vat C is saturated with ammonia it forms a fairly concentrated solution of sulphate of ammonia. In the first phases of the operation this acid is greatly diluted by the steam mixed with the vapour

of ammonia, but as the acid heats considerably, the steam traverses it without combining with it. The solution of sulphate of ammonia is not, however, concentrated enough to crystallize on cooling, that is why it is evaporated in flat becks of lead, iron, or wood heated by a closed coil. This operation must be done with care. Under the action of heat the organic matter contained in the solution exercises a reducing action on the sulphate of ammonia; ammonium sulphite, hyposulphite and sulphide of ammonium are formed, two substances which strongly attack the metal of the apparatus; as, moreover, this reduction gives rise to a great loss of ammonia in the form of ammonium sulphide which is very volatile, the workman ought to moderate the heating as soon as he perceives the smell (of rotten eggs) of this latter product. Evolution of $(NH_4)_2S$ or H_2S infringes the alkali act. When the solution is sufficiently concentrated it is run into iron tanks, where the ammonium sulphate is deposited as it cools. The mother liquor which flows from the crystals still contains an important proportion of ammonia. Sulphuric acid is added to it and it is again distilled; finally it also can be evaporated and recrystallized. The mother liquor from this

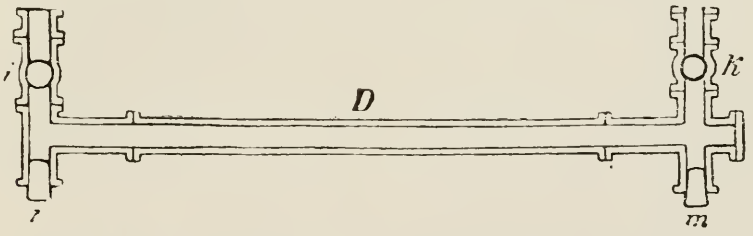


Fig. 41.—Details of Pipe communicating with the two Stills of Fig. 40.

second evaporation contains too many impurities again to yield sulphate of ammonia by crystallization. However, it still contains a notable proportion of ammonia in different bodies derived therefrom, that is why it is run into the boiler B to extract the ammonia by distillation after adding milk of lime.

Mallet's Still.—This still is shown in Figs. 42 (front view) and 43 (longitudinal section of one of the batteries). It consists of two batteries of stills AB, BB, CC, DD, which work parallel and impart to it, as will be seen further on, great capacity of production. The stills A and B are fitted with a perforated double bottom, in which the ammoniacal liquor, to which milk of lime has been added, is brought to the boil. They are fitted with an agitator to keep the liquor in motion, to prevent it from adhering to the bottom. The ammoniacal vapours given off from these stills pass into the stills C and D, likewise filled with ammoniacal liquor, where they are washed to deprive them of their elements more volatile than ammonia. From the still D they pass into a coil 25 m. (82 ft.) long, the spirals of which are contained in the receiver F, where they are

cooled by ammoniacal liquor. The condensed ammonia flows into the vessel S, and from there into the collecting reservoir Y. The uncondensed vapours pass through a pipe, traversing the lid of the vessel S into an air refrigerator T. From there into the pipes U, fitted with a safety arrangement, which sends them into an absorption vessel placed behind R. The unabsorbed bad-smelling gases are absorbed by special arrangement. We have followed the progress of the ammonia driven off from the liquid under the

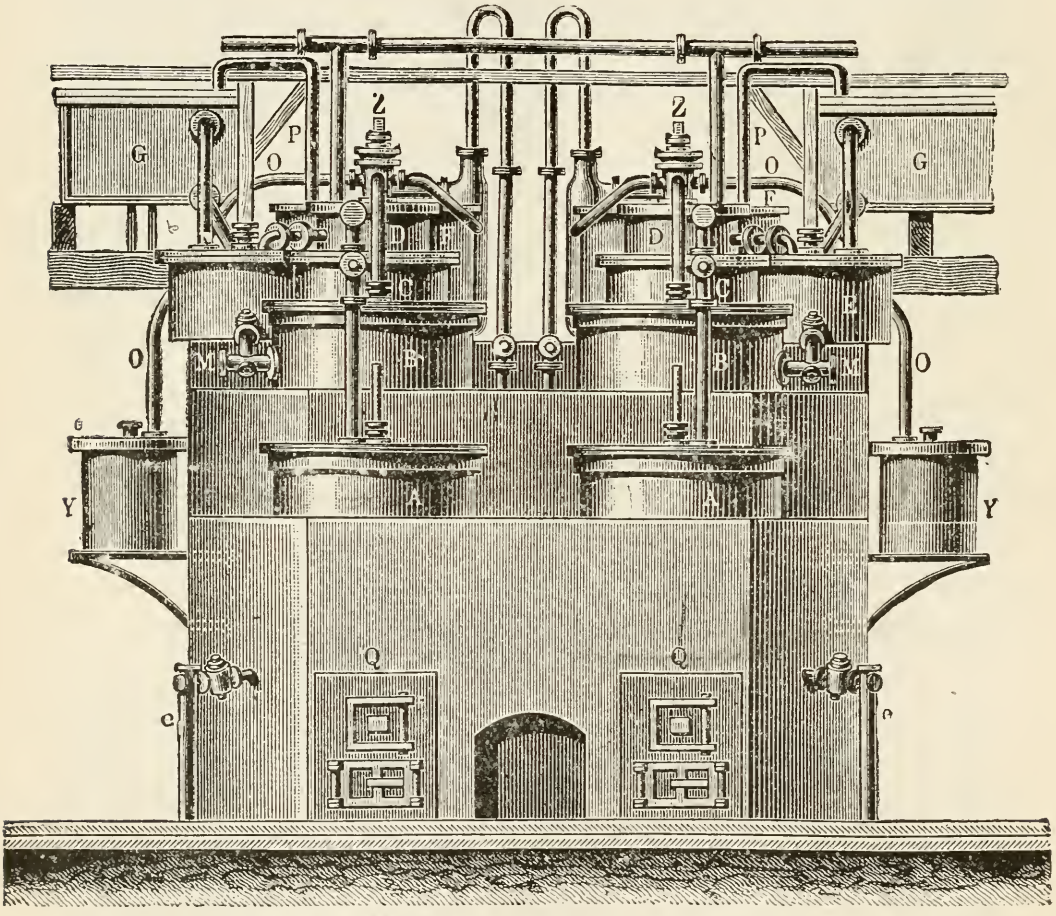


Fig. 42.—Mallet's Ammonia Still (front view).

influence of heat; let us now follow the inverse movement, i.e. that of the ammoniacal liquor used to feed the stills. This ammoniacal liquor is contained in a reservoir higher up, whence it passes into the measuring vessel G, through tap *a*; from that apparatus it first passes into the condenser F, where the steam brought by the coil gives up its heat to it and warms it; the ammoniacal vapours given off rise into G by the pipe P. The stills A, B, C, and D are fed by communication pipes not shown in the illustrations. As already

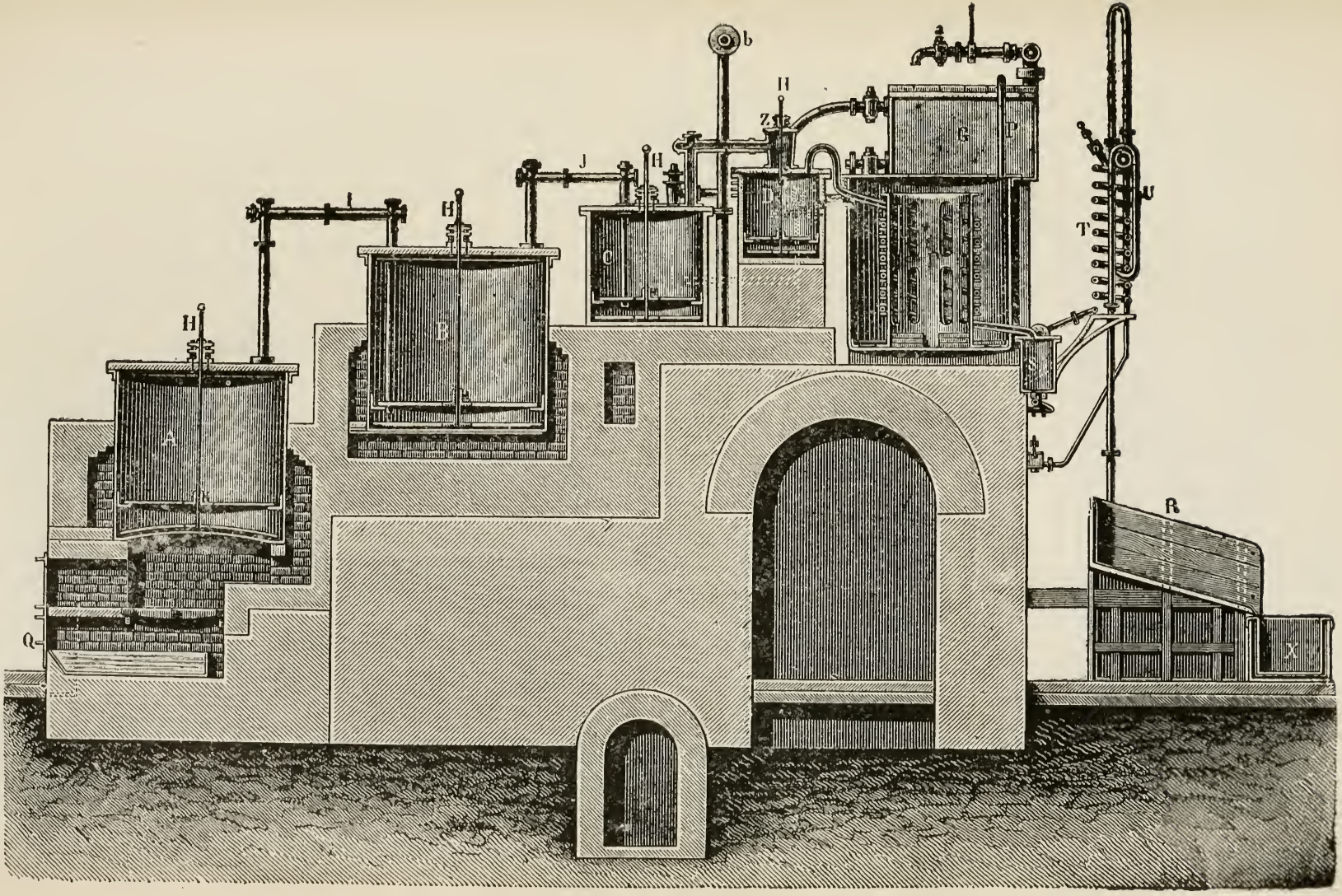


Fig. 43.—Mallet's Ammonia Still (longitudinal section).

said, the ammoniacal vapours formed in the pans A and B pass into C and D, then into the condenser. The milk of lime is prepared in the reservoir E, whence it passes into the still B by the pipe M. The still A is emptied from time to time, say every three days; the discharged liquid is then replaced by an equal quantity of ammoniacal liquor coming from the stills B, C, and D. The condensed water in the vessel Y may be emptied into the vessel D through the pipe O. For that purpose the three-way tap Z, which brings two of the pipes entering D into communication, is fixed in the right place for the ammoniacal vapours not to pass into the refrigerator F, but into the reservoir Y.

The absorption vessel is lead lined and filled with the sulphuric acid intended to make sulphate of ammonia. The latter is put to drain in R, the mother liquor flows into X, and thence into the absorption vessel.

The air refrigerator T is only used when it is desired to make liquor ammonia. In the manufacture of sulphate of ammonia it is replaced by a cylinder 10 ft. high and 20 in. in diameter, into which the pipe bringing the ammoniacal vapours dips, until just above the bottom. By fitting the cylinder with an overflow pipe, matters are so arranged that it is always one-third full. The water from the overflow pipe flows into the collecting vessel Y. The furnace is shown in Q. The combustion gases first impinge on the still A, and then pass under the still B. The Mallet stills at work at the Villette Gas Works produce 10 tons of sulphate of ammonia daily.

Lunge's Still.—This still is based on the same principle as the preceding, but it is much more simple; *a* is the *still*, *b* is the pipe leading the vapours to the condenser *c*. The refrigerator *d* is fed by ammoniacal liquor; it communicates with the still by the pipe *e*. The contents of the still may be run out by the pipe *f*, which is closed when the still is at work by a valve *g*. The lime which is deposited at the bottom of the boiler is again brought into suspension by the agitator *h*. The tap on the pipe *i* is opened when the liquid from the refrigerator *d* is heated to the point of giving off ammoniacal vapours; the latter pass through *i* into the pipe *b*, and afterwards into the coil *c*, mixing with the vapours coming from the still *a*. When the vapours have traversed the washer *k* they pass by the pipe *m* fitted with a safety arrangement into the lead-lined wood absorption vessel *l*, containing sulphuric acid to absorb the ammonia. The acid flows from the reservoir *o* through the syphon *p* into the absorption vessel *l*. Its arrival is regulated so that the liquid in the absorption vessel is always acid. The vapours given off collect under the hood *r*, whence they are forced into the chimney or burned in the furnace. The sulphate of ammonia deposited at the bottom of the vessel *l* is emptied by a bucket hung to a chain and counterpoise *t*.

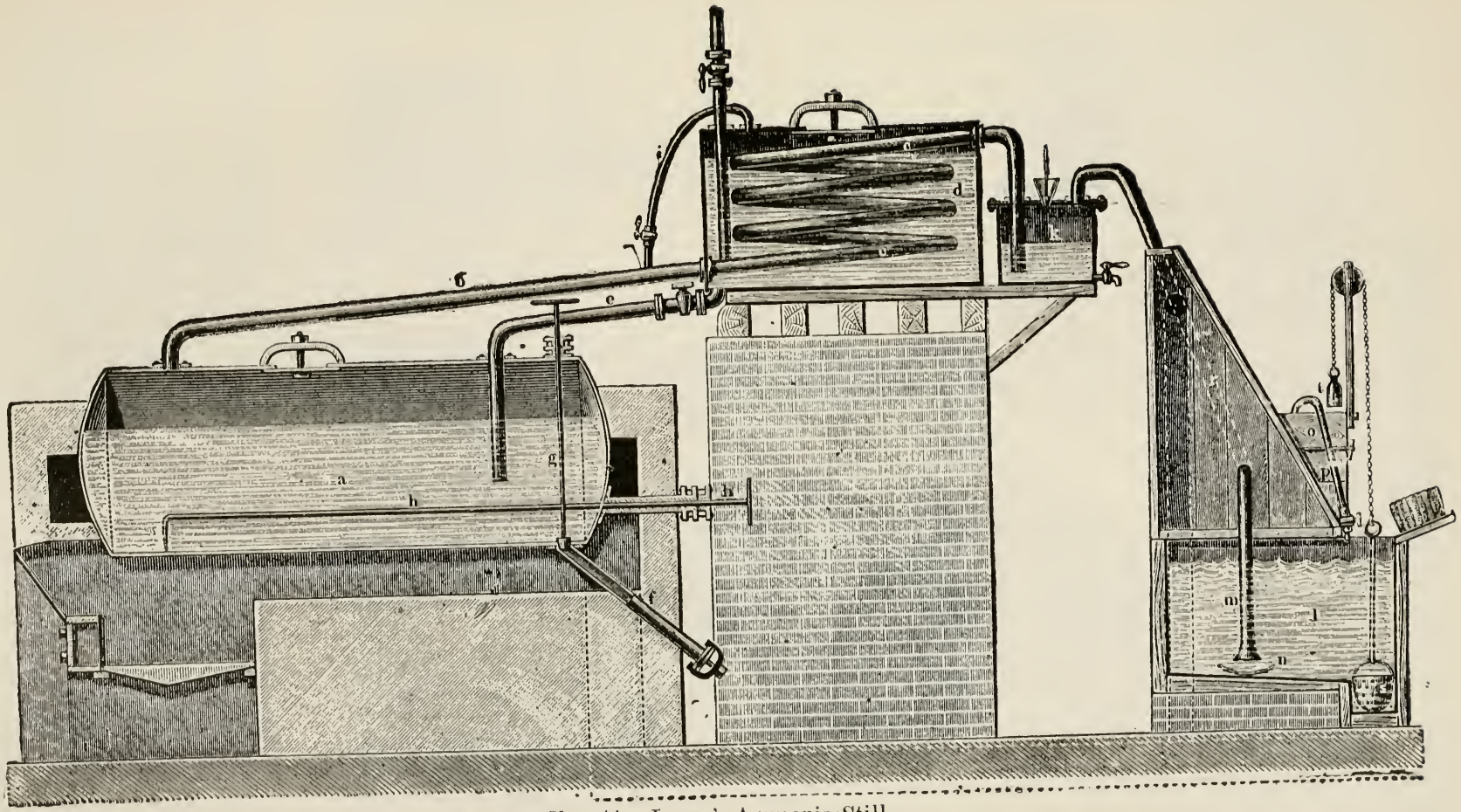


Fig. 44.—Lunge's Ammonia Still.

Steam Stills.—The *intermittent*, naked fire stills have been replaced by *continuous* stills fitted with a rectification column similar to those used in alcohol distilleries. Such a column, the working of which is uniform and continuous, renders it possible to work much more economically. Amongst the best known stills

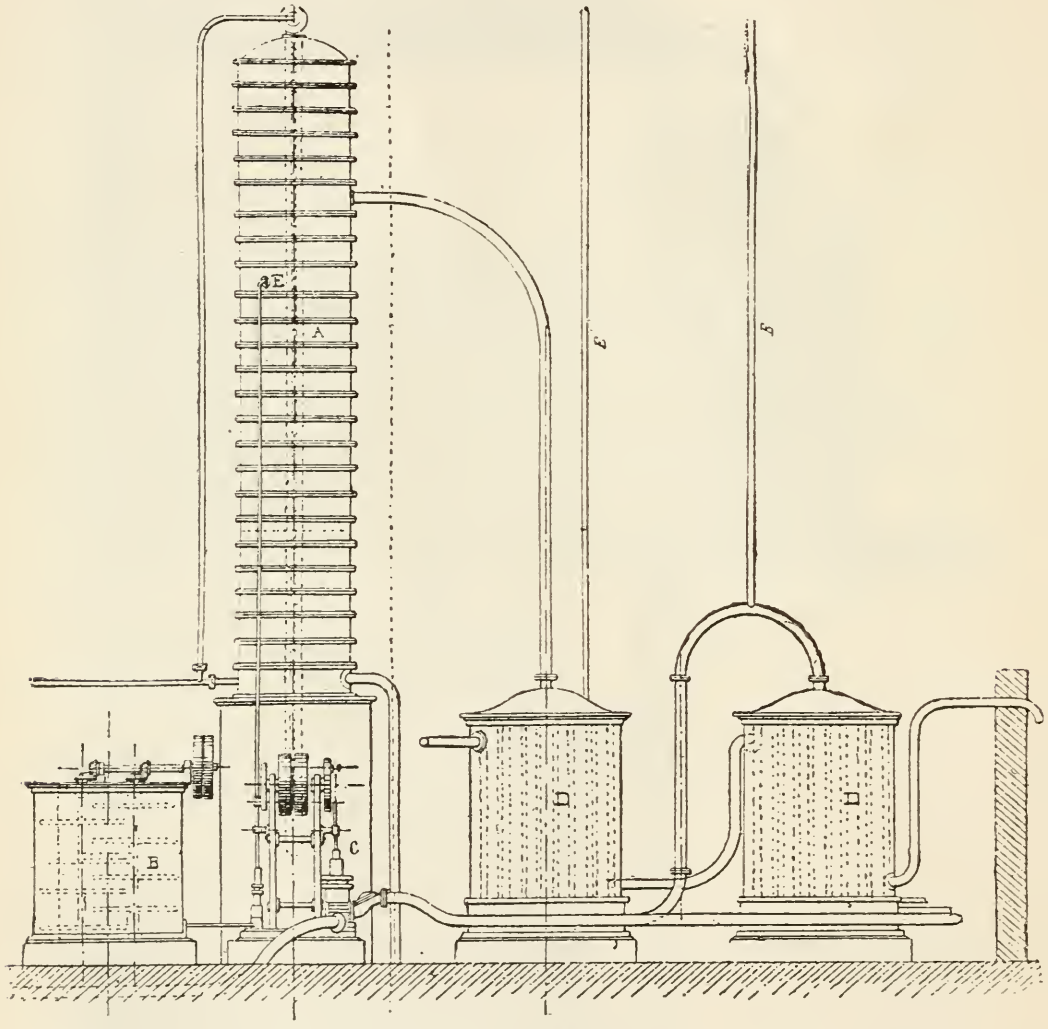


Fig. 45.—De Lair's Still.

A. Distilling column composed of circular segments of cast-iron. B. Milk of lime mixer. C. Milk of lime pump. D.D. Exchange heaters. Entrance of milk of lime into column. E. Gas escapement.

of this nature, those of De Lair, Feldmann, and Gruneberg may be quoted.

Feldmann's Still. — The ammoniacal liquor contained in a reservoir *a* flows into a measurer *b*, passes through the pipe *c* fitted with a valve *r* into a tubular reheater *j*, rises through *d* into the rectifier A, and meets the vapours which deprive it of all

volatile ammoniacal compounds. Finally it arrives in the decomposition vessel B, into which milk of lime contained in the vessel H is run from time to time by means of the pump G and the pipe *n*. The ammoniacal compounds which have resisted the action of steam are decomposed in B, where the liquid is kept in motion by a jet of steam injected through the pipe *p*. The ammoniacal liquor treated by the milk of lime, the non-volatile elements of which are thus entirely decomposed, flows out in a continuous

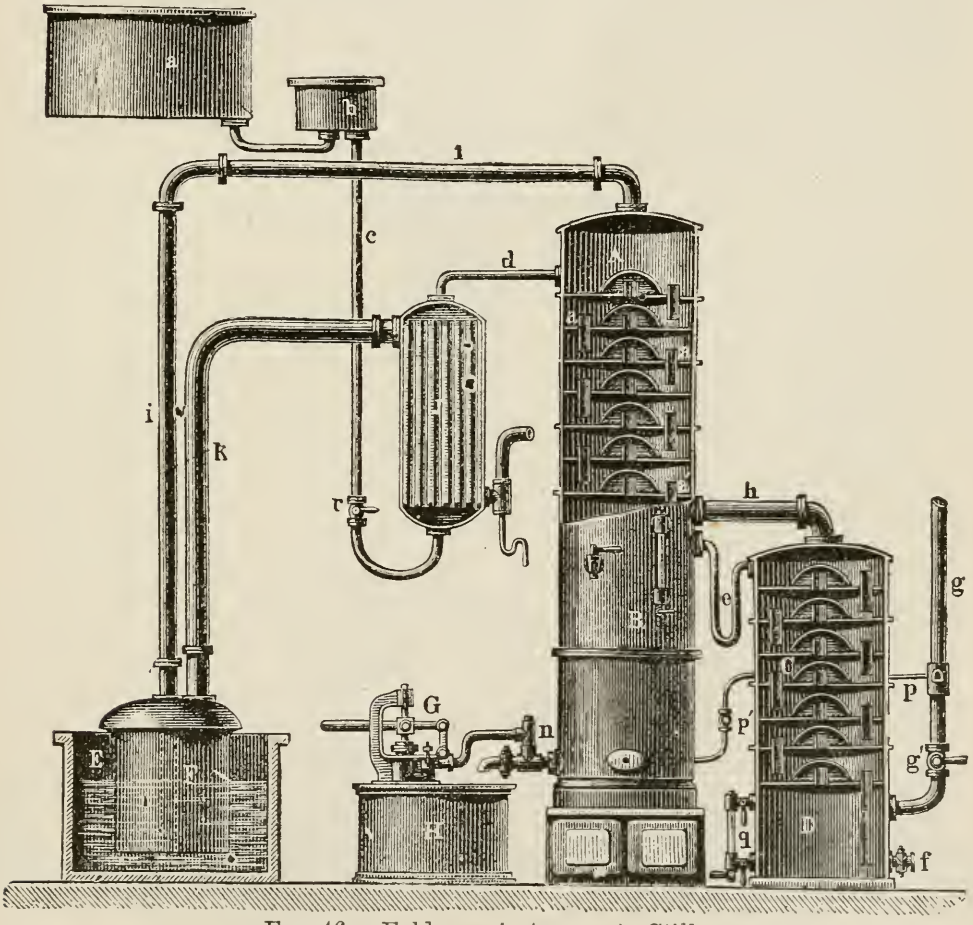


Fig. 46.—Feldmann's Ammonia Still.

manner through the pipe *e* into a small column C, where the free ammonia is volatilized. The water, completely exhausted, collects in D fitted with a water level *q*, and flows in a continuous fashion into *f*. The steam enters all the parts of the apparatus by the pipe *g*, fitted with a valve *g'*; it passes through the column C, the pipe *h* and the column A, the pipe *i*, and finally charged with ammonia it enters the saturation vessel F, filled with sulphuric acid and cooled by the water of the reservoir E. The gases not absorbed

in F, viz. steam, CO_2, H_2S, are led by the pipe *k* into the tubular reheater J, where they transfer their heat to the ammoniacal liquor. The sulphuric acid contained in the vessel F is sufficiently concentrated for the sulphate of ammonia formed to precipitate completely after saturation. The disengagement of heat accompanying the combination of ammonia with sulphuric acid gives rise to very energetic evaporation, which considerably facilitates the precipitation of the sulphate. Feldmann's stills work very economically and are very much used in Germany. A large-sized still of this type distils 44,000 gallons of ammoniacal liquor in twenty-four hours.

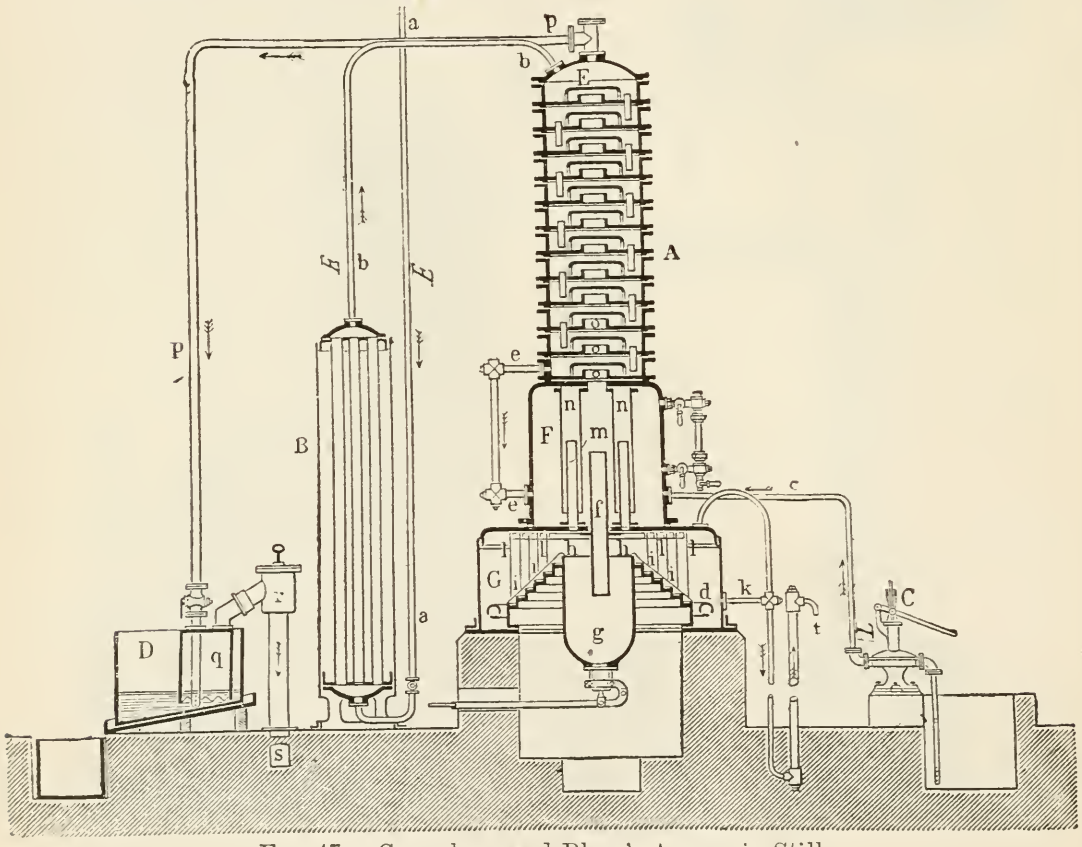


Fig. 47.—Gruneberg and Blum's Ammonia Still.

Gruneberg and Blum's Still.—The liquor first passes into a tubular reheater B through the pipe *a*; it then ascends into the column A in E by the pipe *b*; it descends the column from plate to plate to meet the steam; then it passes through the pipe *e* into the boiler F, which contains milk of lime, where the combined ammonia is liberated. The liquid which fills the boiler F rises above the level of the pipe *f*, flows into the mud pocket *g*, passes out at *h*, spreads over the gradations of the column *i*, and runs away by the pipe *k* and the orifice *t*.

In the boiler G the water which only contains a portion of the ammonia liberated by the lime comes in intimate contact with the steam, which is injected through the perforated coil *d*. The steam forced by the concentric sides of *l* to rise along the gradations of the column becomes charged with the ammonia it meets, and passes by the pipe *m* into the pipe *n*, which forces it to traverse the liquid of the milk of lime chamber. The ammoniacal vapours afterwards rise into the rectifier, and finally when they are entirely deprived of water they pass through the pipe *p* into the saturation vessel D. The bad-smelling non-condensable gases are collected in the bell *q*, whence they return through *r* and *s* into the reheater; finally they are burnt in a special furnace. The milk of lime is injected by the pump C into the still through the pipe *c*. Stills of this type have been installed capable of treating 5500 to 7920 gallons of ammoniacal liquor in twenty-four hours. They work economically and require little superintendence.

Remarks.—Continuous stills should be entirely of cast-iron. Copper and bronze should not be used, for they are rapidly corroded by the ammoniacal vapours. The presence of ammonium sulphide in the ammoniacal liquor is very annoying in work. This body gradually corrodes even cast-iron vessels. Therefore, iron reservoirs are sometimes replaced by cement ones. According to Kunheim, gas liquor may be freed from sulphur by a strong current of air, the effect of which is to decompose the ammonium sulphide into H_2S and NH_3.[1]

Manufacture of Sulphate of Ammonia from Urine.—Amongst organic matters putrid urine is one of the most important sources of ammonia. The putrefaction of urine gives rise to the formation of carbonate of ammonia, seeing that urea CON_2H_4 contains two molecules of water. An adult produces on an average 30 grm. of urea, which corresponds to an annual production of 24·2 kg. or 53·2 lb., nearly ½ cwt., of sulphate of ammonia.[2]

As the carbonate of ammonia is very easily decomposed into CO_2 and NH_3, it has been thought advisable to utilize it in the manufacture of sulphate of ammonia. Figuera used the following apparatus for the purpose. In the furnace V is the boiler W, which propels steam into the wrought-iron cylinders C C′ containing about 100 hectolitres (2200 gallons) by the pipes T and T′. The two cylinders are charged with putrid urine. The ammonium carbonate vaporized passes by T″ into the lead coil *e* in vat A; it condenses with the water and passes in the state of solution into the vessel S filled with sulphuric acid, where it is converted into sulphate of

[1] But ammonia distillers are prohibited in Great Britain from letting H_2S escape.—Tr.

[2] Say, for the whole 5,000,000 odd population of London, 2,500,000 cwt. of sulphate of ammonia, worth say £1,250,000, run into the Thames and carried out to sea annually.—Tr.

ammonia. The liquid used to cool the coil in the vat A, containing about 250 litres (55 gallons), is putrid urine, which thence passes into the cylinder C and C′ by a pipe not shown in the figure. The boiler W contains the hot liquor not entirely exhausted from a previous distillation which still contains a small proportion of NH_3. The pipe T leads the steam into the vessel C; *m* is a pipe which dips a little above the bottom of the boiler whilst its other end passes outside the factory roof; *n* is a safety pipe which indicates at the same time (by the ascent of balls of froth) if the level of the liquid has lowered to the end of the tube *m*; *o* is a discharge pipe. The vessels P and P′ are to retain the abundant froth which would otherwise contaminate the distillate. To ascertain the level of the froth in the vessels P P′, these are fitted at different heights with three lateral apertures closed by wood on plugs, through which the froth flows when the plugs are removed; when the distillation which

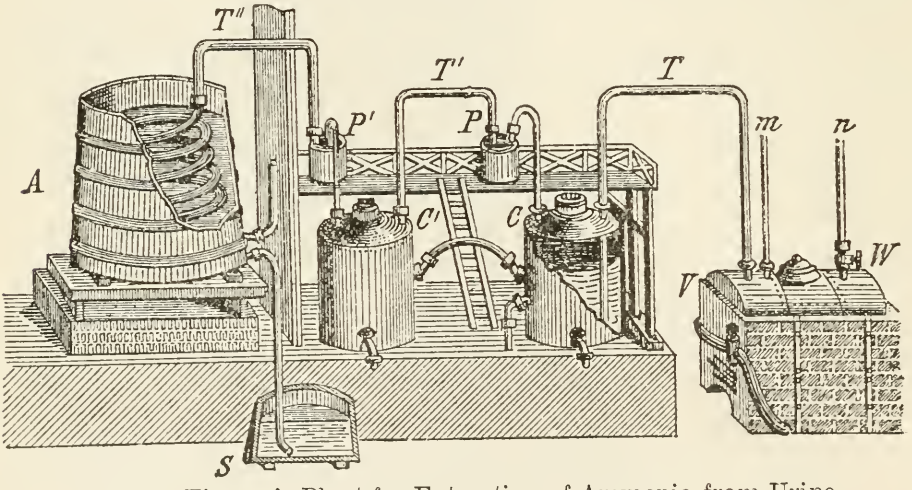


Fig. 48.—Figuera's Plant for Extraction of Ammonia from Urine.

lasts about twelve hours is finished the boiler *o* is emptied and again filled with the urine contained in C C′.

Utilization of Peat in the Manufacture of Ammoniacal Salts.—For some years greater and greater efforts have been made to utilize peat in the manufacture of sulphate of ammonia. The abundance of the raw material, its cheapness and the facility of its extraction, and finally the unlimited outlet for commercial nitrogen as manure, are all factors which are in favour of the use of peat.[1]

Numerous processes have been invented for the extraction of nitrogen from peat. (1) In that of Van Heefien (1905) the pulverized substance washed with HCl, then with ordinary water until

[1] Deposits of peat are by no means so extensive as generally imagined. There are few peat mosses that would keep a distilling plant of large capacity at work for a couple of years. Peat company promoters would lead us to believe that every bog was a peat moss and a mass of solid peat.—Tr.

neutral, is placed in the receivers arranged in diffusion battery style, where they are methodically exhausted by water charged with ammonia, which facilitates the solution of nitrogenous matters. The gas is extracted from the final product for re-use. But only nitrogen in humic acid combination is obtained, which restricts its use in the manufacture of chemical manures, and the value of which does not exceed that of organic nitrogen (*vide infra*). The value of the organic nitrogen of manures is increased by converting it into ammoniacal compounds. Rickmann, D.R.P. No. 8238, submits peat previously heated to from 350° C. to 800° C. to the action of a mixture of air and steam; but, as already mentioned, a great part of the ammonia is destroyed at such high temperatures, so that the yield is very poor. Waltereck, French patent 345,399, obtains better results by heating peat mixed or not with other carbonaceous matters to a maximum temperature of 300° to 500° C., at which the mass is not incandescent. The mixture of air and steam heated to 300° C. (572° F.) is brought in contact with the peat in vertical iron retorts surrounded by refractory stones. The temperature of the mass rises naturally up to 400° C. (752° F.); the heating of the arriving gas is stopped, the heat produced by the reaction being more than sufficient to maintain the heat at a suitable degree. The arrival of the air is so timed as to oxidize completely the carbon of the charge in three to six hours. The quantity of steam should be proportional to the temperature. The inventor, cert. of addition No. 6407, has been enabled to suppress all fuel by replacing the steam with very finely pulverized water in the current of air injected. The ammonia is extracted from the combustion gas by cooling with or without bubbling; ammoniacal liquors are thus obtained utilized as usual. As Muntz and Laine have determined, yields much superior to those by dry distillation have been obtained where the coke retains 1 per cent of nitrogen; a peat containing 2 per cent of nitrogen abandons 1·6 to 1·8 per cent in the ammoniacal liquor.

Muntz and Girard distil peat (previously dried and crushed [1]) in a current of superheated steam. Water gas, mixed with ammoniacal vapours, tars, pyroligneous products, are produced. The combustible gas is used to heat the retorts; the distillation products treated by bicarbonate of soda residue from the extraction of the ammoniacal liquors yield NH_3 and CO_2, re-entering into the manufacture; and acetates of lime and soda, methylic alcohol, and analo-

[1] The drying of peat is a costly item even when air dried. But here in wet seasons in many peat districts it cannot be air dried; resource must therefore be had to artificial drying, and the whole manipulations—making and maintaining road to moss, casting, spreading, turning, cocking, carting, stacking, and crushing the peats—bring peat too near the price of coal for its treatment to prove remunerative.—Tr.

gous products, accumulate in the mother liquors of the bicarbonate of soda, from which they are extracted by distilling the mixture of alcohols, NH_3 neutralizing NH_3, and then redistilling. Finally, the residue from the distilled peat may be used as a substitute for animal charcoal in the manufacture of clarifying and purifying filters. The ammonia is present in the ammoniacal liquors more especially as carbonate.

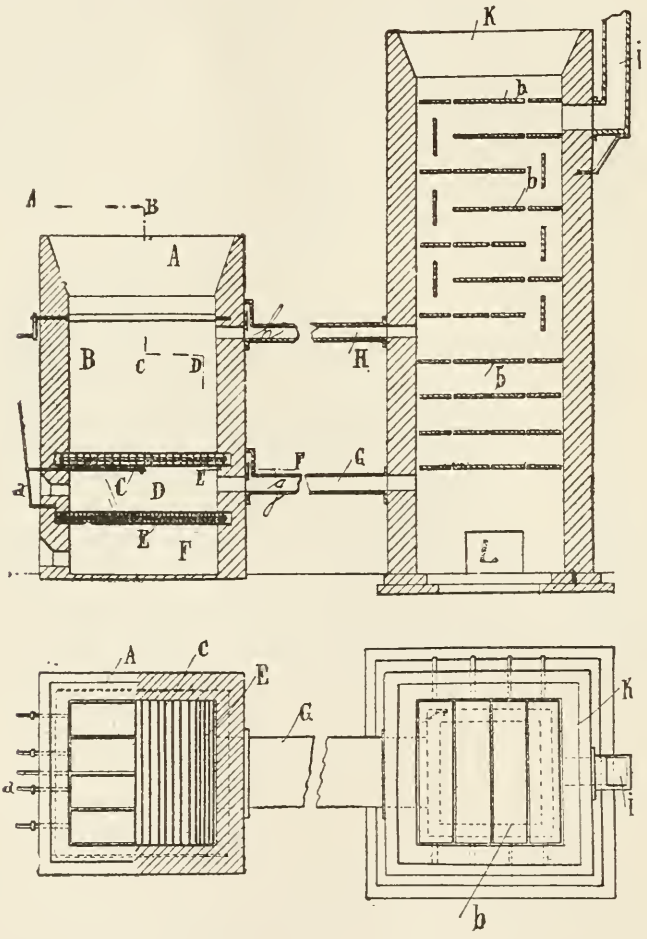


Fig. 49.—Gaillot and Brisset's Oven for Recovering Ammonia from Peat.

Gaillot and Brisset convert the organic nitrogen of peat into ammonia by slow combustion. The dry or moist peat—pure or mixed with other nitrogenous matter—is crushed then fed into the hopper A of the oven (Fig. 49). The bottom of the hopper consists of a grating of flat rotary bars after the style of the laths of a metallic venetian blind, in such a way that if it be turned on its axis the charge passes entirely into the oven, which is at once closed. The combustion of the peat is fractionated into two stages; at first it

passes from the top of the furnace into the distilling zone, where it is dried and then heated to convert it into a sort of coke. The gases produced charged with steam ammonia and tar pass into *h*. The barred grate C enables the admission of the incandescent coke into the zone of combustion to be regulated—a real furnace, where the peat burns before passing to the ash-pit. The ammoniacal gases, dry and very hot, pass out by the pipe utilized as a heating surface for the concentration of the ammoniacal liquors. Dampers F as well as shaking grates C and E enable the progress of the combustion to be regulated.

Recuperation of the Ammonia.—For the manufacture of fertilizers it is advantageous to substitute for simple condensation a method of fixing the ammonia in a form immediately utilizable as a manure. The porosity of peat gives it a considerable absorptive capacity. Bacqua and Lorette use it to absorb the ammonia from the distillation gases. These pass into chambers containing perforated boxes arranged as baffles and filled with a mixture of peat, sawdust, and sulphuric acid, and are there deprived of all their ammonia.

Gaillot and Brisset use pure peat impregnated with acid solutions or mixed with superphosphate of lime as an absorbent. Their recuperator (Fig. 49) consists of a tower K, divided into ten stages by wide oscillating flat bars driven independently, so as to be able to regulate from the outside the forced methodical circulation of the absorbent of whatever nature it may be. The arrivals respectively of the hot and cold gas produced in their ovens already described are in G and H at heights calculated so that the space H I is sufficient for the gases escaping by the chimney I not to contain more than traces of ammonia, and that the path G H suffices to dry perfectly the manure reaching the discharge door of the oven L.

Muntz and Girard collect ammonia by condensation and bubbling, purify the ammoniacal liquors by distillation, then treat them by NaCl. Ammonium chloride and insoluble bicarbonate of soda are obtained; the carbonation is finished by a current of carbonic acid from the residual bicarbonate, then it is filtered. The calcination of the product enables the ammonia to be recovered, and gives CO_2 utilized for the next carbonation. The filtered solution contains an excess of NaCl and ammonia, as ammonium chloride and carbonate. The carbonate is separated by distillation, and calcined at a higher temperature. NaCl equally soluble in the hot state as in the cold crystallizes; it is separated, and there is finally obtained a very concentrated solution of ammonium chloride, which is crystallized. The product may afterwards be refined or used directly as manure.

Manufacture of Sulphate of Ammonia from Peat by the Mond Process.—After numerous unfruitful experiments on the utilization of peat, Dr. Caro has applied the Mond process, by which poor coals

are utilized, not only to produce gas to drive motors, but also to utilize their nitrogen as sulphate of ammonia by giving to the gas producers an appropriate arrangement. Experiments made in this direction at Stockton by Mond for the utilization of peat have given very satisfactory results, and as a sequel to these an experimental factory was installed in Germany capable of treating 50 to 60 tons of humid peat daily. That factory commenced to work in 1908 by utilizing 350 tons of peat placed at its disposal by the Prussian ministry of agriculture. The peat, a portion of which had been delivered as far back as 1907, and another part in the spring of 1908, after having been kept in the open air was very wet; certain parts showed a percentage of 42·47 per cent of water, others 65·70 per cent. The average percentage of nitrogen calculated on the dry sample was 1·05; the percentage of ash was, on an average, 3 per cent with the daily treatment of 45 tons of peat with 42 to 47 per cent of water. 1000 kg. (one metric ton) of dry substance yielded in the gas producer 2800 cubic metres of gas, containing 17·4 to 18·8 per cent of carbonic acid by volume, 9·4 to 11 volumes per cent of carbonic oxide, 22·4 to 25·6 volumes per cent of hydrogen, 2·4 to 3·6 volumes per cent of methane, 42·6 to 46·6 volumes per cent of nitrogen, and only traces of oxygen. The combustible elements of the producer gases rose, therefore, to 36 to 39, and their calorific intensity was, on an average, 1400 calories per cubic metre. For peat, with 65 to 70 per cent of water, the percentage of carbonic acid and the volume of gas was higher, but the total amount of combustible elements fell to 28·6.[1] Now, as the gas from

[1] It cannot be too much insisted upon that there is peat and there is peat. On the one hand, it may approach lignite, but peat of that nature only occurs in pockets and is the remains of buried timber, etc. Again, there is the fibrous sphagnum peat of bogs, the moss litter style of peat, which holds water like a sponge, and which when cast contains 200 to 300 per cent of water, and which when dry shrinks to about a quarter of its bulk. This is the most widely distributed form of peat, but even it is not distributed to the extent imagined. If any of those inclined to invest in peat companies saw the gap made in a peat moss by the extraction of 300 tons of *dry peat*, they would more than hesitate. But when the average investors see an analysis of peat with 2·8 nitrogen per cent = 3·4 per cent of ammonia, closely approaching that of bones, they begin to imagine what a grand thing peat is and what a wonder it has never been utilized before. The fact of the matter is, however, that every now and then history repeats itself, and there is a rejuvenescence and recrudescence of peat patents, so that now in 1910 we may exclaim with the editor of the "Chemical News" in 1860, "yet another peat patent". But if matters have improved in extracting ammonia and gas from peat since 1860, so also have methods improved in regard to coal, and it is not a question of the products that can be got from peat nor of their calorific strength alone, but it is a question of the cost of production. The Stockton experiment is out of the reckoning altogether, and it is not fair to compare gas and ammonia from peat by the water gas process with the same from coal by coke ovens. The author has himself shown that Mond obtained 32 kg. of sulphate of ammonia per ton of coal. With his process applied to peat 40 kg. were obtained, calculated to the dry peat, or about half that

blast furnaces, with 20 per cent of total combustibles, are still utilizable to drive gas engines, the gas, with 28·6 per cent of combustibles, yielded by such a wet peat might also be used to drive explosion motors, and, with greater reason, for heating. A measured sample of the normal gas, with 36 to 39 per cent of combustible elements, was taken to a 50 H.P. gas motor, fitted with a Prony brake, and it was found that for one effective H.P. it was necessary to use 2·4 cubic metres. Tar dust was almost completely absent. As 1 ton of peat yields 2800 metres of gas, that gives a yield of 1160 horse-hours, and as the gas, escaping at 500° C., suffices to produce the steam required for the producers, and as the air-pumps and water-pumps, as well as the scrubber, require little force, one is safe in counting on a yield of 1000 horse-hours per ton of dried peat, that is, on an amount of energy sufficient to combine 50 kg. (say 1 cwt.) of atmospheric nitrogen under the form of cyanamide of calcium, CaN_2H_2, or from 16 to 20 kg., 35·2 to 44 lb., of nitric acid.

But the agricultural utilization of peat is still more advantageous if the ammonia be extracted from the gas generated in the gas producers. If all the organic substance of the peat be gasified in a mixture of air and superheated steam, a hydrolysis of the nitrogenous substances of the fuel is produced, i.e. of the peat, and this hydrolysis is so energetic that, if the gas be washed in a sulphuric acid scrubber, 77 to 80 per cent of its nitrogen is obtained as sulphate of ammonia. The peat burnt at Sodingen which contained 1·05 per cent nitrogen gave an effective yield of 40 kg. (88 lb.) of sulphate of ammonia per ton. A small lot of peat—gasified in the Stockton factory—which contained 2·8 per cent of nitrogen in the dry substance gave likewise, according to the experiments of Dr. Caro, as much as 110 kg. (242 lb.) of sulphate of ammonia per ton, whilst coal generally contains 1 per cent of nitrogen. No account was taken of the secondary products of the combustion of peat tar for instance, which is obtained in somewhat important quantity, as well as acetic acid and wood-spirit, because time was awanting to estimate the value and importance of these bye-products, and afterwards because it was thought that the gasification of peat would not develop on a large scale unless the two chief products which it yielded, motor gas and sulphate of ammonia, offered sufficient profit without it being necessary to instal complicated equipment for the treatment of the bye-products. If afterwards the treatment of the bye-products appears to be profitable, it is believed that it will always be time to examine it, but at the present it has not been taken into account. To finish, let us quote an arrangement for the extraction of ammonia

on the wet peat. It would thus take 100 tons of the weather wet peat to produce a ton of sulphate of ammonia.—that is, 8 tons of this weather wet peat had to be treated to produce £1 worth of sulphate of ammonia.—Tr.

from combustion gases, which is the subject of the American patent 816,035 of 5 March, 1907. The hot gases from the combustion products of coke ovens, etc., enter by a tube A into an apparatus containing the tubes of a refrigerator B, and from there into a second refrigerator D, by the pipe C. A pump G aspirates the cooled gas from the refrigerator D by the pipe F, and propels them into the tar separator H. The gases freed from tar return by the pipe I into the refrigerator D, and from there by the pipe K into the refrigerator B. In the refrigerators B and D the gases are reheated by the hot gases which enter by the pipe A and surround the tubes. From there the gases pass through the pipe L into an acid tower M, which is filled with coke or analogous matter, on which a reservoir N delivers acid as a fine rain. The gases thus freed from their ammonia pass through a pipe O, into a refrigerator P, and can then be used for different purposes. The ammonia extracted from the crude gas and combined with acid is absorbed in the refrigerator D at the same time as the water. The liquid separated in B and in D is evacuated by the pipe Q into the reser-

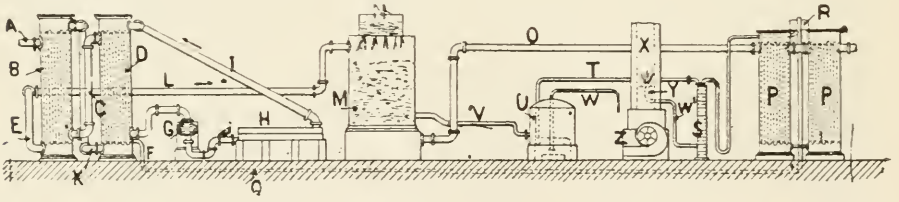


Fig. 50.—American Plant for Recovery of Ammonia from Combustion Gases.

voir B, and from there it is directed into a distilling apparatus S. In that apparatus it is distilled by steam over milk of lime; the ammoniacal vapours pass by the pipe T into a saturation reservoir U, which is fed at the end of the pipe V with liquid formed in the acid tower M. The sulphate of ammonia which is deposited on the bottom of the apparatus U is evacuated in a continuous manner by the injector W. The residuary water from the still is conducted by the pipe W′, terminated in the form of a rose, into the chimney X, the draught of which is stimulated by the fan Z. Sulphate of ammonia obtained by the processes described is the only kind used in agriculture. According to its percentage of moisture it contains 20 to 24 per cent of ammonia, which corresponds to 77 to 93·2 per cent of sulphate of ammonia, or of 16·5 to 19·8 per cent of nitrogen.

Crude Ammonia from Spent Oxide.—The material used to purify coal-gas also contains spent oxide, and furnishes a product called crude ammonia (*crud d'ammoniac*). Although ammonia can be extracted from it in the pure state by treating it like gas liquor, generally it is simply concentrated by evaporation. A product is

then obtained which should only be employed as manure with great precautions. Some years ago Maercker analysed a product of this kind, under the name of crude ammonia. He found the following products :—

TABLE LXX.—ANALYSIS OF SPENT OXIDE FROM GAS WORKS.

	Per cent.	
Moisture	8·7	
Sulphate of ammonia	17·8 = 5·3	per cent nitrogen.
Insoluble nitrogen compounds	5·4 = 1·8	,, ,,
Ferrous sulphate	15·6	
Sulphur	10·7	
Cyanogen compounds	1·2	
Ferrous oxide and ferrous sulphide	22·3	
Lime organic matter	14·8	
Sand, clay, etc.	3·5	
	100·0	containing 7·1 per cent N.

Amongst these compounds the sulphate of ammonia is the only fertilizing material ; the insoluble nitrogenous compounds, the sulphur, the lime, the sand, the clay, are inert materials ; whilst the ferrous sulphate, the sulphide of iron, and the cyanogen compounds, are plant poisons. These substances should not be employed as manure under any pretext.[1]

Another crude ammonia of this nature exceedingly dangerous, and also from an English source, and put on the market under the name of brown sulphate of ammonia, was analysed by C. Schuman. This product contained :—

	Per cent.	
Water	4·86	
Sulphate of ammonia	14·87 = 3·15	per cent nitrogen.
Rhodanate of ammonia	73·94 = 27·24	,, ,,
Sand	6·23	
	99·90	with 30·39 per cent N.

The rhodanate [ammonium sulphocyanide] contained therein is exceedingly poisonous to plants, and before using it, it is necessary to ascertain if it is exempt from this body.

The departmental laboratory of Chalons-sur-Marne analysed in 1907 a somewhat large number of crude ammonias from different sources. The composition of some of the samples examined is given in the following table :—

[1] Green vitriol has been used as a manure for stimulating etiolated plants for nearly a century.—Tr.

TABLE LXXI.—PERCENTAGE OF DIFFERENT NITROGEN COMPOUNDS PRESENT IN A SERIES OF SAMPLES OF SPENT OXIDE FROM GAS WORKS.

	Total Nitrogen. Per cent.	Nitrogen Soluble in Water. Per cent.	Ammoniacal Nitrogen. Per cent.	Nitrogen of Sulphocyanic Acid. Per cent.	Insoluble Nitrogen. Per cent.	Moisture. Per cent.
1	2·69	0·817	0·22	0	1·87	25·52
2	5·61	1·718	1·01	0·157	3·93	14·95
3	2·96	0·89	0·37	0	2·07	2·52
4	7·08	4·32	2·89	0·789	2·76	15·68
5	3·80	0·198	0·181	0·068	3·61	12·68
6	3·15	0·396	0·321	0·044	2·76	3·20
7	2·75	0·396	0·075	0·307	2·36	11·88
8	5·24	1·519	0·922	0·307	3·73	20·40
9	4·19	2·24	1·19	0·832	1·95	17·32
10	2·56	1·38	0·498	0·540	1·18	4·60
11	6·40	2·90	0·915	0·498	3·50	16·14
12	8·04	4·29	1·547	1·210	3·75	24·57
13	5·43	1·58	0·99	0·195	3·85	5·72
14	9·70	6·34	4·185	0·950	3·36	5·74
15	6·60	4·42	2·51	1·198	2·18	10·41
16	5·60	1·58	0·697	0·535	5·02	22·67

This table shows that the composition of these crude wastes is very irregular. There seems to be no relation between the different forms of nitrogen to be met with therein. Their appearance, smell, and moisture vary exceedingly, some black, others brown, whilst others present a whole play of colours, from deep blue to almost black, to greenish-blue. Sometimes the smell is sulphurous, sometimes cyanic, at other times the smell of benzine or tar predominates. Their consistency is generally pulverulent, sometimes, however, it is damp, pasty, and manipulated with difficulty. All these variations are explained by recalling the origin of the crude, which is a material for purifying coal gas. Ammoniacal compounds, sulphides, cyanides, come from the gas, also naphthalene and tarry matter varying in proportion according to the coal used and also according to the arrangement of the purifiers, because efforts are made to retain the ammonia and the tar before they reach the crude. The matter used to retain the impurities is not always the classic lime and sulphate of iron, green vitriol, which yields sulphate of lime and oxide of iron; the inert absorbent, generally sawdust, sometimes consists of shavings, or again of earthy matter. The gasworks which delivers the waste has therefore a great influence on its composition, and this influence further increases by the care taken in storing the material as it comes from the purifiers.

Commercial Sulphate of Ammonia.—Commercial sulphate of ammonia contains in round figures 20 per cent of nitrogen. Generally 24·5 per cent of ammonia, the term used in Great Britain, is guaranteed; however, there is generally found salts up to 25 per cent of ammonia.[1] When pure, sulphate of ammonia is white, but it generally contains traces of tar or its derivatives. The yellow colour is often produced by the presence of arsenious sulphide, the green coloration by cyanide of iron, but these colours disappear on drying. It is known that ammonia is converted in the soil by a ferment into nitric acid $NH_3 + 4O = HNO_3 + H_2O$, but this nitrification is only possible if the sulphuric acid of this salt be combined with lime. Commercial sulphate of ammonia should be neutral and contain as a maximum 2 per cent of water; when it contains only 1 per cent of rhodanate of ammonia (NH_4SCN), ammonium sulpho-cyanide, it is injurious to plants, according to Maercker. But these impure products are no longer manufactured. Sulphate of ammonia is dried in a steam dryer, crushed in ball mills with a No. 50 sieve or in Carr's disintegrator. Bags which have contained sulphate of ammonia, like nitre bags, are dried and cleaned by beating or by washing with water; the wash water, if it be not desired to evaporate it, is sent to the concentration pan.

As already mentioned, the strength of sulphate of ammonia may be expressed in two ways. In France it is customary to give the percentage in nitrogen; in other countries, especially in Great Britain, it is given as ammonia, so that the same sulphate has a strength 21·21 per cent or 25·75 per cent according to the designation adopted. To prevent any confusion, it suffices to *multiply the strength in ammonia by the number* 0·8235 *to obtain the corresponding percentage of nitrogen.* Inversely, *by multiplying the percentage of nitrogen by* 1·214 *the corresponding percentage of ammonia is obtained.* The following table gives the calculations for all strengths met with in commerce :—

[1] Pure sulphate of ammonia contains 25·7 of ammonia NH_3. But commercial sulphate always contains free acid and other impurities including moisture. Even good commercial sulphate of ammonia contains enough impurities to stultify the "complete" analysis as usually performed. All the nitrogen is calculated to sulphate, although very evidently it is not all present as sulphate. There are traces of substances with lower equivalents than sulphuric acid, so that when the nitrogen is calculated to ammonium sulphate, the free acid determined and the combined acid also as well as the moisture, no manipulation of the figures will bring them down to 100 per cent. A trace of this "rhodanate" of ammonia, so rich in nitrogen, would explain all this, and the particulars given in the following paragraph throw still further light on the subject. The re-inventor of a back titration process for testing sulphate of ammonia took no account of free acid! Needless to say, that when facts like the above were also brought before him, he could not grasp their significance. An accurate and complete analysis of even fairly pure commercial sulphate of ammonia is not so simple a matter as at first sight appears. It shows great lack of skill and judgment to combine the extraneous nitrogen in sulphate of ammonia with the free acid, and thus report a larger percentage of sulphate of ammonia than is actually present.

TABLE LXXII.—TABLE FOR CONVERSION OF NITROGEN PER CENT INTO AMMONIA PER CENT AND VICE VERSA.

Percentage of Nitrogen.	Percentage of Ammonia.	Percentage of Ammonia.	Percentage of Nitrogen.
1 × 1·214	1·214	1 × 0·8235	0·8235
2 ,,	2·429	2 ,,	1·6470
3 ,,	3·642	3 ,,	2·470
4 ,,	4·856	4 ,,	3·294
5 ,,	6·070	5 ,,	4·117
6 ,,	7·284	6 ,,	4·935
7 ,,	8·498	7 ,,	5·764
8 ,,	9·712	8 ,,	6·588
9 ,,	10·926	9 ,,	7·411
10 ,,	12·140	10 ,,	8·235
11 ,,	13·354	11 ,,	9·058
12 ,,	14·568	12 ,,	9·882
13 ,,	15·782	13 ,,	10·705
14 ,,	16·996	14 ,,	11·527
15 ,,	18·210	15 ,,	12·352
16 ,,	19·424	16 ,,	13·176
17 ,,	20·638	17 ,,	13·999
18 ,,	21·852	18 ,,	14·823
19 ,,	23·066	19 ,,	15·646
20 ,,	24·280	20 ,,	16·470
21 ,,	25·494	21 ,,	17·293
22 ,,	26·706	22 ,,	18·117
23 ,,	27·920	23 ,,	18·940
24 ,,	29·134	24 ,,	19·764
25 ,,	30·348	25 ,,	20·587

CHAPTER XIII.

MANUFACTURE OF MANURE FROM ANIMAL WASTE.

Preliminary Remarks.—The utilization of waste of animal origin is of the same economical importance as of human excreta. Like the latter, the products have come from the soil and been paid for in the manure. Unfortunately, these wastes are not collected with sufficient care, in spite of the great facility with which they can be utilized. Vast quantities of blood are annually lost in the slaughter-houses of both large and small towns, where the air is infected by the products of its decomposition. Numerous animal carcases are buried every year, not only through following an old custom, but moreover in order to obey certain prescriptions of the sanitary police. Their conversion into chemical manure is their best disinfection. In this conversion all animal matters are boiled, which not only destroys living organisms, but also the germs of putrefaction and the germs of contagious diseases. Moreover, as animal matters are not long in beginning to putrefy if left to themselves after boiling, manure manufacturers have the greatest interest in avoiding this decomposition, because it always entails a certain loss of nitrogen, its most valuable constituent. This is effected by drying, for dried animal matter can be stored for years without decomposing. By examining the methods used for the manufacture of manures, it will be seen that they not only afford means of making an excellent profit from animal waste, but also of destroying all the contagious germs which they may contain, and that therefore the police regulations which require all animals that have died from infectious disease to be buried, are thus quite contrary to economy as well as to well-conceived hygienic measures. The animal matters rich in nitrogen most often utilized in manure manufacture are—blood, meat (flesh), horn, and leather waste.

Blood.—Fresh blood forms a red thick liquid of density 1·045 to 1·575 (6 to 7° B.) (9 to 15° Tw.). In contact with free air it soon separates into two parts, one solid, fibrous, forms the clot, whilst the other, liquid, constitutes the serum. The clot consists mostly of fibrin, whilst the serum especially contains dissolved albumen (7 to 8 per cent). Blood contains per 1000 parts, 796 of water and 204 parts of solid. The solids consist of:—

191 parts of nitrogenous matter, fibrin, albumen, globulin.
2 ,, ,, fat.
3 ,, ,, extractive.
8 ,, ,, mineral matter.

204

Amongst the mineral matters of blood, mention must be made of chloride of potassium and of chloride of sodium (common salt), and also phosphoric acid, lime, and magnesia. Phosphoric acid forms 9·8 parts; potassium chloride, 46 parts: corresponding to 29 parts of potassium. The composition of blood differs a little according to the animals from which it comes, as the following analyses by Wolff show:—

TABLE LXXIII.—ANALYSES OF BULLOCKS, CALVES, SHEEP, AND PIGS' BLOOD.

	Bullocks' Blood. Per cent.	Calves' Blood. Per cent.	Sheep's Blood. Per cent.	Pigs' Blood. Per cent.
Water . . .	79	80	79	80
Solids . . .	21	20	21	20
Nitrogen . . .	3·2	2·9	3·2	2·9
Phosphoric acid .	0·04	0·06	0·04	0·09
Potash . . .	0·06	0·08	0·05	0·15

Dried Blood.—Up to now (and still at the present time) blood was mostly coagulated in factories by steam in an open pan, adding to it 3 per cent of ferric sulphate solution marking 51° B. (110° Tw.). The coagulated blood was then laid to drain in perforated cases, where it remained for a month, and thus lost 40 per cent of the 80 per cent of the water which it contained. The coagulated and drained product was then dried on hot cast-iron plates in a shelf-oven traversed by hot gases. This mode of operating has numerous drawbacks; odoriferous fumes are given off by the drying itself and bad-smelling fumes owing to the partial decomposition due to irregular heating of the nitrogenous matter. Attempts have been made to remedy this, it is true, by condensing the first and denaturing the second by fire.

Moreover, not only do the arrangements necessary to secure a satisfactory result require continuous supervision, but the manufacturer does not apply them except against his will, as they perceptibly increase the cost of the products without any marked advantage as regards quality. The drying of blood in Donard and Boulet's machine—about to be described—prevents the disengage-

ment of all odoriferous products, and thus avoids costly gas condensation and denaturation processes. Before this new application, this machine was already in use in distilleries to dry dregs, and this use of it was described by the author as far back as 1892. The drying machine (Fig. 51) consists of a horizontal cast-iron cylinder 2·5 m. in diameter by 2·5 m. long—say in round figures, 100 in. × 100 in., representing an interior volume of 12 cm. It rests on two bearings by hollow pivots through which the heating steam enters and the evaporation steam is ejected. The heating steam enters a circular vertical steam chamber which forms the left side of the cylinder. On this side are inserted a series of horizontal tubes closed at the other extremity which form a heating surface of 59 square metres. The machine is fitted with the necessary arrangements for running off condensed water. The pivot placed at the other end of the cylinder communicates by a wide pipe with a double effect vacuum condensing pump into which the evaporation vapour passes. The cylinder is fed and emptied through two manholes. The charge of moist material—containing 55 per cent of water—is 5½ tons. It makes three revolutions a minute.

Method of Working.—The working is most simple. The machine is connected by a pipe with a tank containing the blood, then by means of the vacuum pump the air in the cylinder is rarefied so as to force the blood to precipitate itself by suction. When 5½ tons have been fed into the machine, say an amount equal to ⅓ the capacity of the machine, the aspiration is shut off and the mass is heated under a pressure of 1½ kilos whilst turning the cylinder. The blood is then perfectly coagulated under the influence of the heat without any part escaping from the beating up. After one hour forty minutes to one hour fifty minutes, coagulation is complete. The apparatus is emptied, the magma is run into cloths and pressed under a press mounted on a truck. Each press takes 1 ton to 22 cwt. of dried blood as it comes from the curing machine. After pressure, which is 3 kg., 400 kg. (880 lb.) of cake with 50 per cent of water are taken out; 3½ tons of these cakes are used to feed another machine absolutely identical with the first, but which this time acts the part of a drying machine. In a medium-sized factory a single machine may act both as curing and drying machine.

In factories with two machines the curer is altered by fitting two steam circulation pipes perforated in the portion which dips into the cylinder; and used to bubble in steam during the coagulation, they have the advantage of preventing the other heating pipes from being left bare.

To dry the cakes the vacuum is stopped, for the vacuum pump might entrain a portion of the extremely light powder to which the blood is reduced by drying. During that time the vapours escape through great wooden aspirators passing through the roof. As

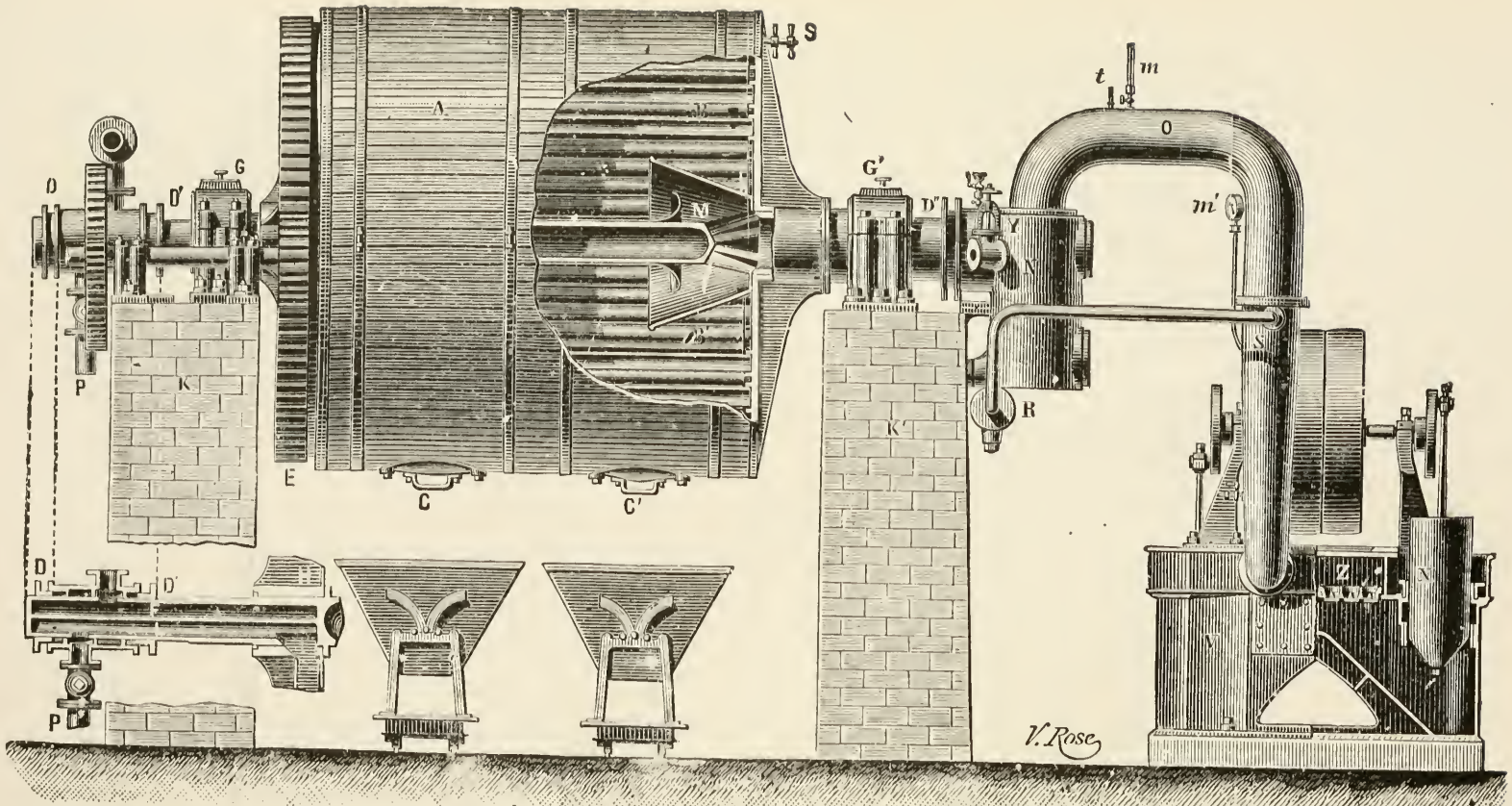


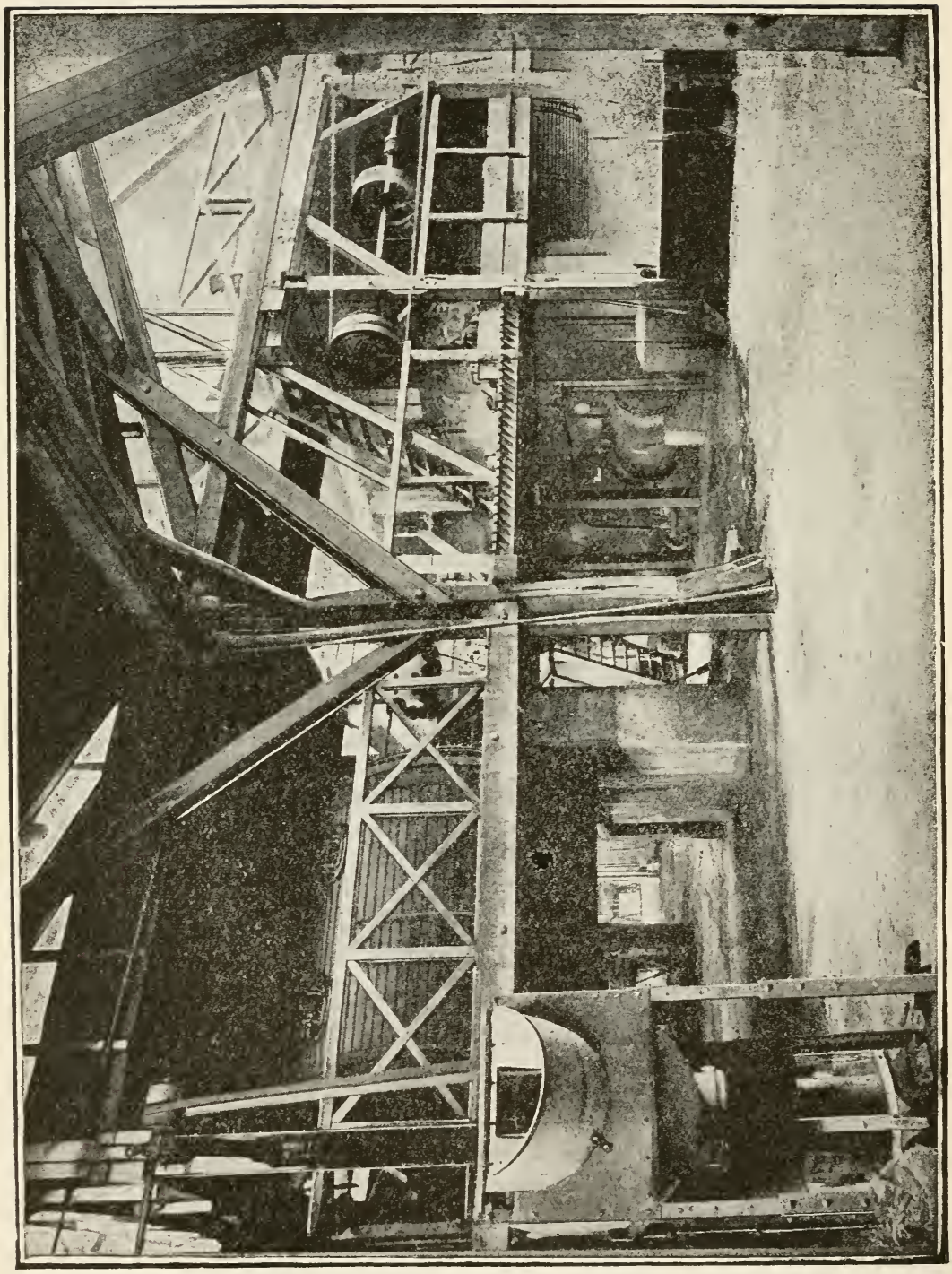
FIG. 51.—Donard and Boulet's Drying Machine.—A, Cylindrical envelope; B, Heating tubes; CC', Feeding and discharging manholes; DD', Stuffing box for entrance and exit of heating steam; D'', Stuffing box for exit of steam extracted from the material being dried; H, Entrance chamber of the heating steam, and exit of this steam when condensed, fitted with a revolving cog-wheel; E, P, Exit of condensed heating steam; GG', Bearings; M, Baffle stopping entrained matter; N, Dust box; O, Pipe leading to condenser; R, Injection pipe; S, Condenser; V, Air pump; X, Piston of pump; Z, Valves; Y, Entrance tap for air; *t*, Thermometer; *mm*, Manometres; *s*, "Cheese-taster" for taking samples.

during the process there can be no alteration of the material, either by fermentation or by superheating, the portion evaporated consists simply of pure water without trace of smell.

Drying lasts six to seven hours and induces the agglutination of certain portions into hard masses so as to obtain an impalpable powder; the dried mass is pulverized in a Carr's crusher completely enclosed in a wooden case and in communication with an aspirator for dust recovery.

All these operations follow each other. The fresh blood is converted in less than ten hours into a powder which is bagged up ready for immediate delivery. As will be seen further on, 1000 litres (220 gallons, say 1 ton) of blood from the Villette slaughter-houses yields with these machines 210 kg., say in round figures 4 cwt. of dried blood. According to multiple experiments made at the Aubervilliers factory, the coal used for all these conversions is estimated at 0·833 lb. per lb. of dried blood. They calculate that in actual practice 5 tons of coal suffice to convert 28½ tons of liquid blood. The motor power is at a maximum for three driers of 15 cubic metres each. The improvement in the yield due to these machines is considerable, as results from the following experiment. After previously mixing, 16 metric tons of blood, coagulated by ferric sulphate, and containing 62 to 65 per cent of water, was divided into two lots; the first lot of 8 tons, dried in a hot-air oven, yielded 2·555 metric tons, say a yield of 31·5 per cent. The lot of 8 tons, treated in a Donard machine, gave 3½ tons of dried blood, say a yield of 45 per cent. The percentage of water in the dried blood from the two treatments was perceptibly equal, 15 to 16 per cent. The difference of yield, 13·5 per cent, shows the loss the dried blood undergoes by overheating in the hot-air oven above-mentioned.

Meat Meal.—As far back as 1863 manure was made at Aubervilliers (Seine) from dead animals or animals slaughtered in the department of the Seine and its neighbouring departments. The fat was first extracted for the knackers and the rest was converted into manure. The flesh was cooked by steam, then pressed to extract the fat, dried, and ground. The bones were also boiled, then dried and crushed to a fine powder. Finally, with the entrails, the boilings and the residues of the organic matter, composts were made of low nitrogen content. They were mixed with the residues from the manufacture of fat (? greaves), ground mineral phosphates, bone residues, fur, etc., were added, and the whole piled in a heap and drenched with blood and boilings. These substances, difficult to assimilate, especially ground mineral phosphates after an active and prolonged fermentation, undergo slow conversion which renders them assimilable. The composts mixed in different proportions with rich substances, dried meat meal, dried blood or crushed bones, enable manures of all strengths to be prepared containing 1·5 to 2·5 per



cent of nitrogen, and up to 25 per cent of phosphate. The mineral phosphates were coprolites. From time to time the compost heap was watered with sulphuric acid to avoid loss of ammonia and to render the phosphates soluble. The manure most rich in nitrogen so manufactured contained 12 per cent and a little phosphate. By mixing it with bone dust and alkaline salts, Dulac prepared a manure containing 8 per cent of nitrogen, 12 per cent of phosphates, 15 per cent of potash salts, soda, magnesia, etc. This manure was sold at 24 francs the 100 kg. (say £10 a ton). The Aubervilliers factory continues to use meat waste for the manufacture of manures, but it has considerably improved its processes, as will be seen. The blood in powder tests 13 per cent of water and 13·2 of nitrogen; it treats per month on an average 3500 casks of 185 litres (40·7 gallons), yielding 155 metric tons of dried blood.

Drying Blood by Lime.—Recently a simple process has been used to dry blood and to reduce it to a fine powder. This process consists in adding 1½ to 3 per cent of quicklime, which converts it into a solid cake which may be dried in the air without putrefying, and finally gives a fine and inodorous powder. This process has the advantage of being capable of being applied everywhere without any plant; moreover, it preserves 0·4 of nitrogen, which otherwise would be lost with the coagulation water. It may likewise be applied in the country by farmers, who thus possess the means of manufacturing economically an excellent nitrogenous manure.

Boiling Meat.—Butchers' waste of all sorts, skinned animals cut into pieces, are first boiled in lead-lined vats. The lid of the vat has in its fixed half a square opening to which a wooden sheath fits, the other half, movable around two hinges, is used to feed in the materials to be treated. Each vat is charged with—

Meat, etc.	800 kg.
Water	150 ,,
Sulphuric acid	50 ,,

The vat being charged, the lid closed, and steam turned on, the boiling lasts about twelve hours. The vertical wooden sheaths on the top of the vats form real draught chimneys branching into two large horizontal collectors which end in a masonry turret; there the vapours from the boiling are constantly precipitated by the play of a fan. The tower contains a filter of coke, constantly moistened by a stream of water. The aspirated vapours are in great part condensed owing to the freshness of this water; they then pass with it into the drain. After twelve hours the vats are opened, the floating fat removed, in the proportion of 10 to 20 per cent according to the nature of the debris, then the bones and the flesh completely disintegrated. The liquors from the boiling are drained through special piping into two large tanks. The tallow, as it

comes from the vats, is more or less dark, according to the impurities contained in the raw material. Three classes are distinguished, white tallow, yellow tallow, and green tallow. The paler it is, the more it is valued by candle-makers and soap-makers. It is again boiled so as to skim it, and eliminate the impurities which accompany it. It is afterwards run into casks ready for delivery. After removing the tallow, what remains in the boiler (disintegrated flesh, bones completely detached, the largest of which are removed) is put into a press which removes 15 per cent of water and dried. The Butchers Union of Paris, in its Aubervilliers factory, uses two systems of driers, one *naked fire*, the other *steam*. In the *steam* drier, Donard's system (Fig. 51), drying lasts seven hours at the most. The *naked fire* drier resembles an enormous coffee roaster, fitted with an agitator; it is driven by the central shaft; its furnace is arranged like that of a boiler; drying lasts at least ten hours; the amount of coal consumed is enormous. Donard's dryer is much more economical and has the great advantage of yielding an absolutely inodorous powder. The drying operation is complicated by the comparatively large quantity of fat which the meat and bones retain after boiling, and which has not risen to the surface with the tallow. This fat renders the substance to be dried tacky; it is inflammable, especially when air is blown over it at a high temperature. The products coming from the dryer are brought on to a sorting sieve which throws the bones on one side, and delivers the finely powdered meat on the other side; the latter is bagged up for delivery. By the use of Donard's dryer all this work can be done in less than twenty-four hours, from the time the meat entered the factory until it is bagged up in the state of powder; 100 kg. of pressed material yield 33 kg. of dried matter; 100 kg. of pressed material correspond to 140 kg. of original material. Meat meal is sold according to its percentage of nitrogen. The following is its average analysis:—

TABLE LXXIV.—COMPOSITION OF MEAT MEAL.

	Per cent.
Water	8
Tallow	3
Nitrogen	4·6
Phosphoric acid	15

The liquors from the boiling are collected into two cisterns, where they are left to deposit for several days. Their muddy deposit, somewhat rich in organic matters, is taken up by a *montejus* and poured over a very vast area with raised edges, to let it drain better, then mixed with meat from the boilers or put directly into Donard's dryer. At the Aubervilliers factory they treat 805 tons of meat, etc., per month, which yield 15·8 per cent of tallow, 150 tons of dried meat, and 50 tons of bones.

M. A. Louis has organized at Caen an interesting application of Aimé Girard's process, for the destruction and disinfection of carcases and animal debris by means of sulphuric acid. Louis uses likewise slaughter-house and butchery residues. In 1889, his first year of working, Louis made 483 tons of manure containing 16 to 18 per cent of phosphoric acid, 2 per cent of nitrogen, and 5 per cent of potash; in 1900 his manufacture had risen to 930 tons.

Louis' method of working consists in dissolving the animal matter in sulphuric acid, and saturating the pasty mass so obtained by phosphate of lime in powder, which finally yields a nitrogenous phosphate.

Commercial Meat Meal.—The meat meal of commerce is a mixture of meat meal and bone meal. It is made from the waste from the manufacture of extract of meat; in South America also from the carcases of animals, knackers' meat, by steam heating, drying, and grinding. The greater part of the meat meal is marketed as Fray Bentos guano; it contains 6·5 to 7·5 per cent nitrogen and 17·18 to 11·14 of phosphoric acid. Finally, meat meal is rendered soluble by sulphuric acid.

Horn.—Horn is met with under different forms in commerce. The horns of ruminants are generally very pure, and contain dry and free from bone 13 to 14 per cent of nitrogen. Whalebone waste, when not in too small fragments, is almost equal in value. Horn and whalebone turnings and shavings are less esteemed, because they are generally mixed with wood shavings and other sweepings of the workshop. Their nitrogen content rarely reaches 7 to 8 per cent. Hoofs are richer in nitrogen than ground horn. They generally consist of pure horn; on the other hand they are often wet and soiled by excreta. Hair, wool, wool rags, old felt, and feathers have the same value as horn. But great care must be taken in buying, because it is difficult to determine the impurities of all sorts which may be mixed therein. In the pure state they contain 11 to 13 per cent of nitrogen; as sometimes delivered to the factories they only contain 5 to 6 per cent. Wool dust, from the combing and spinning of wool, is not of a nature to inspire much confidence. It rarely contains 6 per cent of nitrogen, often only 3·4 per cent of that element. To serve as manure all these materials must be reduced to a fine powder. But even when apparently dry they are so tenacious that it is impossible to grind them. Wool dust itself already in a fine powder cannot be ground finer. That is why they are submitted to a special preparation, which consists in roasting them or in heating them in a closed vessel. To roast horn, it is spread on a cast-iron plate or in a shallow pan, which is heated without interruption so as to avoid overheating and loss of nitrogen. The matter assumes a dark colour, and when it is cool it is brittle and easy to crush. When it is a case of horn turnings, it suffices to

heat them for some time on the roof of a dryer. The roasting may easily be done in a closed vessel into which superheated air or combustion gases are injected. Horn is steamed in a digester. A digester is nothing but a horizontal or vertical boiler heated by steam (Fig. 53). In Fig. 53, *a* is the steam pipe fitted with a valve *b*. On the top is a steam escape valve *c*, safety valve *d*, and a short piece *e* intended for a steam gauge; *gg* is a double bottom of wrought-iron. The shape and the size of the digester vary considerably and depend on the size of the factory. However, it is well to keep to certain rules. Thus a wide somewhat low digester

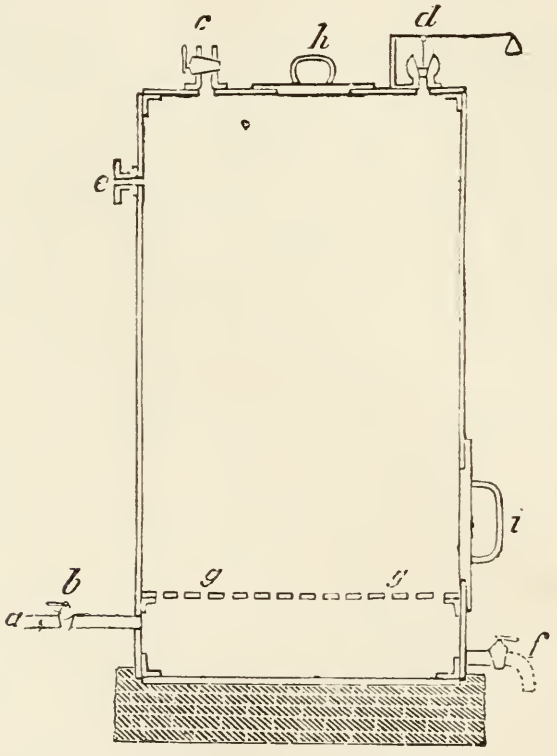


Fig. 53.—Digester for Treating Horn, Leather, etc.

generally runs cheaper, and works more economically than a tall narrow one, because it condenses less steam on its surface.

The digester being charged with horn through the manhole *h* is closed hermetically, the steam valve *b* is opened and steam of two to three atmospheres injected. It condenses at first until the whole mass is heated. The heating lasts two hours for horn in large pieces. When the operation is finished the valve *b* is closed and the apparatus left to itself for some time, and finally the steam valve *c* is opened. When the pressure in the digester has fallen to almost the atmospheric pressure, the digester is emptied.

To do this the liquor formed by the condensation of the steam is run off through *f*. It holds a little dissolved horn in solution; then the lower manhole *i* is opened and the horn withdrawn. When properly boiled, the horn is softened through and through and forms an elastic mass, like rubber. It is dried in a dryer, and then forms a black pliable vitreous mass which is crushed in a bone crusher; that is the way ground horn of commerce is obtained. In the pure state, it has a greenish or greyish-yellow colour, and contains 13 to 15 per cent of nitrogen. Other analogous materials are treated along with the horn. Horn shavings, wool waste, etc., occupy a great volume, and it would take a very large-sized boiler to treat them apart, that is why they are mixed with horn to fill the empty spaces between the large pieces, at the risk even of slightly diminishing the percentage of nitrogen in the product. The condensed water (horn liquor) contains 1 to 2 per cent of nitrogen; it thus has a certain value, but as its treatment would be costly it is best to add it in the manufacture of bone dust. Attempts were made to let it putrefy, and then distil it to recover the ammonia, but this method was soon abandoned. The steaming of horns has many drawbacks. It expends much fuel and labour, and a loss of nitrogen in the condensed water. Finally, the work injures the health of the workmen. There is in fact disengaged from horn during the digestion a very volatile organic substance, which strongly attacks the mucous membranes, especially the workmen engaged in emptying the digester and who consequently have to come in contact with the steamed horns, but up to now nothing has been found to replace this method, because ground horn rendered soluble by steam is of much greater agricultural value than raw horn. It has been seen that the horn dissolves partially in the water condensed from the steam, and that without decomposition it so far proves that it passes to the soluble condition at least partially. Ground horn thus rendered soluble possesses a great absorbent capacity for water, whilst ground raw horn repels water, and cannot be moistened, and as putrefaction requires the help of water, it follows that the soluble horn will decompose more easily, and produce a more rapid and more sure fertilizing action than raw horn. From the preceding, it follows that the use as manures of powdered horn and wool dust which have not been treated by steam should be abandoned, for in the raw state these materials cannot be crushed to the requisite degree of fineness for the rational application of concentrated chemical manures.

Leather Waste.—Tanners' and curriers' waste can be bought cheap when they are unfit for glue manufacture; their nitrogen content is very variable, even when not affected by moisture or sand. Thus sole leather in the pure state and perfectly dry often only contains 4 to 5 per cent of nitrogen. The cutting and waste of new leather from saddlers' and shoemakers' shops have a higher

value ; they contain 7 to 11 per cent of nitrogen, deducting moisture. Chemical manure manufacturers often treat them in the same way as horn, roasting or steaming in a closed vessel, and grinding. The roasting of tanned leather renders it friable without perceptibly modifying its chemical properties. Steaming under pressure dissolves it to a great extent. The leather liquor is sometimes so concentrated that it takes the form of gelatine, and the amount of ground leather finally obtained scarcely renders the half of that fed into the digester. This method, therefore, is not economical. Moreover, steamed leather has only a low value as a manure, for the tannin in the tanned leather prevents the decomposition of the animal matter in the soil, and is only partially destroyed by the heat. The powder obtained from roasted leather is even worse. It is true that the manufacturer again finds in it the greater part of the nitrogen contained in the raw material, and which varies from 5 to 9 per cent. There has already been described, in discussing the preparation of bone dust, a process of preparing leather which is more advantageous both for the manufacturer and the farmer. Another method of treating woollen rags, leather waste, etc., was the subject of British patent No. 26,780 of 22 December, 1905. Raw materials, such as woollen rags, leather waste, previously moistened, if need be, are fed into a horizontal cylindrical receiver and treated by sulphuric acid which falls on them drop by drop, by means of a pipe running the length of the cylinder. At the same time a rotary motion is imparted to the cylinder whilst injecting hot gases from a furnace, then the materials are drenched with salt water, well mixing the whole, and continuing the heat. If leather waste be principally used, it is well to add finely ground phosphate of lime to the acid water. The vapours disengaged by the material are propelled by a pump into a condensation tower lined with bricks, washed by a jet of finely divided water. The non-condensed gases are directed into a filter bed of moss litter, and from there it escapes into the atmosphere ; the final product is discharged into a pit and reduced to a fine powder.[1]

Comparative Value of Different Nitrogenous Manures.—Peruvian guano is the most active of nitrogenized organic manures. Popp has examined the action of the nitrogen of organic manures compared with that of nitric nitrogen. In his experiments he used all sorts of organic manures, dried blood, horn dust, castor meal, ground raw bones, fish guano, meal, meat meal, Bremen poudrette, wool dust. According to the agricultural experiments which he executed, he indicates the ratio which exists between the action of the different manures. Under the cover of this remark, the following are

[1] But using 120° Tw. acid heated to 140° F., 4 cwt. of raw leather or 2 cwt. leather and 2 cwt. shoddy can be got into each ton of compound manure and so well dissolved as not to be seen when the den is opened. So why all this unnecessary labour and expense ?—Tr.

the approximate efficiency values of these manures, nitrate being taken as 100:—

TABLE LXXV.—SHOWING AGRICULTURAL VALUE OF NITROGENOUS MANURES (NITRATE).

Dried blood	70
Horn dust	70
Fish guano	60
Castor meal	60
Meat meal	60
Bremen poudrette	55
Ground bones	55
Krottnauer organic manure	45
Blankenburg manure	43
Distillery spent wash-salts	40
Wool dust	25
Concentrated cattle manure	20
Ground leather	10

The value of the dissolved organic manure is 23 per cent of that of the nitrate. Popp has, moreover, remarked that in every case the organic nitrogen is first converted into ammonia; he was not able to determine the effect of the lime. Complete conversion of organic nitrogen into nitric acid did not occur in any case. In the most favourable instance of 100 parts of organic nitrogen, 72 parts were converted into nitric acid; that is the case especially with dried blood. The nitrogen of horn dust was converted in the proportion of about 57 per cent, and the nitrogenized organic manure in the proportion of 24 per cent. Horn dust thus acted more slowly than dried blood, and the nitrogenized organic manure about half as quickly. Neither in this case was the effect of the lime in the conversion observed. In conclusion, Popp has calculated the value of the nitrogenized organic manure compared with that of nitrate of soda, the latter calculated at 35·25 francs, all expenses included. He values 1 kg. of nitrogen in such organic manures as follows:—

TABLE LXXVI.—SHOWING COMPARATIVE AGRICULTURAL MONEY VALUE OF NITROGENOUS MANURE IN FRANCS PER KILOGRAMME.

	Francs.
Dried blood	1·4
Horn dust	1·4
Fish guano	1·2
Castor meal	1·2
Meat meal	1·2
Bremen poudrette	1·1
Bone dust manure	1·1
Krottnauer organic manure	0·9
Molasses salts	0·8
Dissolved nitrogenized organic manure	0·4
Lutzel guano	0·7
Wool dust	0·5
Concentrated cattle manure	0·4
Ground leather	0·2

CHAPTER XIV.

RECOVERY OF NITROGEN FROM DISTILLERY SPENT WASH. MANUFACTURE OF CYANAMIDE AND OF NITRATE OF LIME.

Utilization of Spent Wash.—General Remarks.—The question of the utilization of distillery spent wash, looking to its great economical importance, has engaged the attention of chemists for a long time. In grain distilleries the dregs are generally filtered, then dried; the spent wash which flows therefrom contains 80 to 100 grm. of nitrogen per hectolitre; and as 100 kg. of grain yield about 3 hectolitres of liquid, the loss of nitrogen is 1 to 1·250 kg. per hectolitre of alcohol manufactured, say 1 to $1\frac{1}{4}$ lb. per 10 gal. of 100 per cent alcohol. In beet distilleries the loss in nitrogen is also very considerable; the fermented wash issuing from the distilling column contains 100 to 160 grm. of nitrogen per hectolitre. Finally, the spent wash from the distillation of molasses and sucrate liquors contains 1·4 per cent of nitrogen and 9 per cent of salts. Now, if the spent wash be simply incinerated, to extract the salts from it according to a process already old, all the nitrogen, of which the money value is superior to that of the potash, is lost. If in a molasses distillery they calculate on a yield of 9 per cent of salts, it will be seen that there is extracted from 1000 kg. (a metric ton) of molasses 90 kg. of salts, say 198 lb., at 40 per cent of carbonate, worth 38 centimes the degree, say 13·68 francs, say 11s., and that there is lost by incineration all the nitrogen, of which 75 per cent at least is recoverable, say 11 kg. (22·42 lb.), worth 1·50 francs the degree, say 16·50 francs, or 13s. 2d.

It will be seen that the problem of the recovery of nitrogen from these residues deserves to attract in the highest degree the attention of distillers. Different processes have been proposed to recover this nitrogen. Attempts have been made to recover it by dry distillation as ammoniacal salts or liquor ammonia. There is then obtained a complex liquid containing tars, methylamines, and other bodies difficult to purify. These processes have not been adopted in actual practice, which would tend to the belief that the financial results did not conform with those which had been expected. Attempts were also made to prepare compound manures from spent wash by adding precipitated phosphate of lime, and inert

matters, generally lime, in somewhat larger quantity up to 40 per cent. But the fertilizing elements in the products so obtained are present in proportions but little acceptable to farmers, and the presence of inert matters rendered their transport charges heavy.

Winck has tried to utilize the nitrogen of spent wash as manure. His process consists in concentrating the spent wash to 40 to 42° B., then to add massive quantities of sulphuric acid. This acid mixture is afterwards neutralized with carbonate of lime, and dried in stoves. The addition of acid and of carbonate favours the drying, the presence of sulphate of lime renders the mass more porous, more easy to treat. The product obtained contains 3 to 5 per cent nitrogen and 12 to 14 per cent of potash. Riviere proposes to separate potash from concentrated spent wash by hydrofluosilicic acid. The organic matter separated from these salts can be evaporated in the same way as in the Vasseux process described below. Effront has likewise introduced a process for separating the organic nitrogen from the mineral substance. This process is based on the observation that the nitrogenous matter of spent wash becomes insoluble when it is treated with acid at a temperature of about 200° C. To the concentrated spent wash acid is added to decompose the *organate;* the mixture is maintained for some hours in stoves at 190° C. A portion of the nitrogen is disengaged and is collected by a fan in the acid. The mass issuing from the stove is crushed, then lixiviated with boiling water. The cooled liquid deposits sulphate of potash. The insoluble residue is dried at 100° C. By this method 8 to 9 per cent nitrogen free from potash is obtained.

Recovery of Nitrogen by Vasseux's Process.—By this method all the nitrogen freed from the greater part of the potash is easily recovered, no noxious principle being generated in the process, which is as follows: The spent wash, previously concentrated to 32° to 35° B., is treated by sufficient sulphuric acid to convert the organates of potash into sulphates. The sulphate of potash formed crystallizes in the midst of the mass; it is separated by decantation, filtration, and centrifuging. This sulphate of potash is afterwards washed and again centrifuged. It is then sufficiently pure and is sold as 75 to 80 per cent sulphate. The organic matters which form the drainage are then dried in special vacuum machines; decomposition is avoided and the distillate glycerine, tar, etc., may be collected.

When drying is complete the mass is run into trucks. It is fluid when hot but soon cools into a mass which is broken up in a crusher. An organic manure is thus obtained containing 6 to 7 per cent of nitrogen and 6 to 7 per cent of potash. This product, almost entirely soluble in water, nitrifies very rapidly in the soil and suits all crops. For every 1000 kg. (metric ton) of molasses treated 150 kg.

of this manure are recovered (in round numbers 3 cwts. manure per ton of molasses) :—

TABLE LXXVII.—SHOWING VALUE AND AMOUNT OF MANURE FROM 1 TON MOLASSES.

1000 kg. (1 metric ton) of molasses yield	*Fr.*
150 kg. (3 cwts.) of organic manure with 6 to 7 per cent nitrogen and 6 to 7 per cent of potash	16·60
75 to 80 kg. (165 to 176 lb., say 1½ cwt.) of sulphate of potash .	14·0
Total	30·60

whilst by the old process only 90 kg. potash salts, worth 13 to 14 francs, were obtained.

Labour is not more heavy than at the potash furnaces and the work is less exhaustive, but there is the extra expense in coal and in acid, which is valued at 5 francs (4s.) per metric ton of molasses. So that the net profit to be drawn from the application of this process over and above the potash salts usually obtained is about 12 francs, say in round figures 10s.

If these figures be applied to a factory working 20,000 tons of molasses, the value of the bye-products to be obtained is 610,000 francs (£24,400), yielding a profit greater by 240,000 francs (£9600) than that obtained from the potash salts alone. These figures show very well the importance attached to the recovery of the nitrogen. Vasseux's process is, moreover, wrought in France and Spain and gives every satisfaction.

Treatment of the Spent Wash by Biological Agents.—Jean Effront has studied a new method of treating spent wash by biological agents. The problem which he set himself was as follows: To find an active substance (diastase) capable, in the conditions of actual practice, of converting the organic nitrogen of spent wash into ammoniacal nitrogen, the form under which it is most easily recovered. This substance, called amidase, exists in brewers' yeast. In the alcoholic fermentation the amidase of yeast and foreign ferments always accompanying industrial fermentation, does not intervene, owing to unfavourable conditions. It only reveals its presence when the yeast finds itself in an alkaline medium and in a non-vegetative condition. After numerous but very simple experiments which demonstrated to him the presence of amidase in yeast and its power of converting amides into ammonia, Effront applied his discovery to the treatment of distillery spent wash. This produces very large quantities of ferment which is deposited at the bottom of the vats; these ferments separated from the fermented liquid before its distillation may be used to treat spent wash. The method of working is as follows: The spent wash issuing from the distilling column is cooled to

40° to 45° C. (104° to 113° F.), rendered alkaline by lime, soda, or salts. One or two kilogrammes of yeast are added per hectolitre and allowed to work for 3 or 4 days at 40° to 45° C. The conversion of amides being finished, the ammonia is separated by distillation or by ventilation (Kestner method). By this latter method the consumption of coal is about 50 kg. (say 1 cwt.) per 100 hectolitres (2200 gal.) treated. By treating molasses spent wash, 100 hectolitres (2200 gal.) yield 40 to 45 kg. (88 to 99 lb.) of nitrogen, representing a minimum value of 40 to 45 francs (32s. to 36s.). In spent wash from beets 100 hectolitres (2200 gal.) yield 10 to 15 kg. (22 to 33 lb.) of nitrogen, worth 10 to 15 francs (8s. to 12s.). The expense in fuel being 1 franc (9·6d.), the actual profit is remarkable.

Treating Spent Wash by Fermentation.—Beer yeast is not the only biological agent capable of converting the nitrogen of spent wash into ammonia. Certain soil ferments likewise possess this property. By innoculating a solution of glutamine by garden soil, the formation of ammonia can be demonstrated. Effront, using plate cultures, has isolated three ferments acting on the nitrogen of spent wash. One of them was recognized as the butyric acid ferment, and Effront has closely examined the conditions which favour its ammoniacal functions. In practice the general course of work with this ferment is analogous to that of the manufacture of alcohol. There is a yeast chamber and fermentation vats; from the ferment there is prepared a leaven equal to 5 to 10 per cent of the total volume of the liquid to be fermented, and it is renewed every twenty-four hours as in distillery brewing. To strengthen the ammoniacal action, recourse is made to aeration to render the liquid strongly alkaline, and to the use of agglutinants, such as sulphate of alumina, which paralyses the development of ferments and produces a change in the function of the cells. For the use of pure cultures, often far from convenient, garden soil which may be very well taken as the point of departure of ammoniacal fermentation, may be substituted. Effront recommends to sterilize this earth mixed with the alkalinized spent wash for an hour at 70° to 80° C. (158° to 176° F.), this sterilization being sufficient to avoid the formation of noxious ferments without destroying those with an ammoniacal function. This soil culture in the spent wash may be used as leaven in the same way as those made from pure cultures on condition that they be renewed somewhat frequently. This process was experimented on at the distillery of Quesnoy-sur-Deule, at the end of the season 1907-8. From the point of view of yield, the work leaves nothing to be desired, and the amount of nitrogen extracted from the spent wash from the manufacture of one hectolitre (22 gallons) of alcohol, may be valued as 12 kg. (26·4 lb.) of sulphate of ammonia (say 1·2 lb. of sulphate of ammonia per gallon of alcohol). In the course of

the molasses season, 25 to 30 kg. (55 to 66 lb.) of sulphate of ammonia were obtained per hectolitre of alcohol, and it has been found that in the distilling column an appreciable amount of glycerine perfectly recoverable is also separated. In treating spent wash by fermentation, almost all the organic matters, including the nitrogenous matter, are decomposed. The spent wash from 370 kg. (814 lb.) of molasses, the approximative quantity to produce 1 hectolitre (22 gallons) of alcohol, yields besides ammonia about 35 kg. (77 lb.) of volatile fatty acids. The acids which pass over on distillation are white and free from impurities. The distillery industry could furnish enormous quantities, and it would be desirable for the trade to find new outlets for them.

The Manufacture of Cyanamide and of Nitrate of Lime.— Atmospheric air is an inexhaustible source of nitrogen. It is calculated that the column of air which covers a hectare (2·47 acres) of ground contains about 79,000,000 kg. of nitrogen (say 79,000 metric tons, which gives 31,600,000 metric tons per acre), equal to 500,000,000 kg. of nitrate of soda (say 50,000 metric tons per hectare or 20,000 tons per acre). But nitrogen exists in the free state in the air, and to render it assimilable by plants, it is necessary to convert it into appropriate compounds. We know that this conversion can be effected by certain bacteria of the soil (leguminous bacteria, etc.), likewise by certain phenomena which occur in nature, such as electrical discharges, especially lightning. But the amount of nitrogen brought into the soil in this way is far from being sufficient to cover the requirements of plants, and vigorous efforts are now being made to capture atmospherical nitrogen under an assimilable form. Experiments made enable us to affirm that such is possible. But all the tentatives made in this direction show that the industrial fixing of atmospheric nitrogen requires the use of great quantities of electrical energy. There are at present two chief methods of manufacture: (1) the Frank and Caro process, (2) the Birkeland and Eyde process. The first consists in combining atmospheric nitrogen dry and deprived of its oxygen with calcium carbide, obtained by fusion in the electrical furnace of equal amounts of coal and lime. The product so obtained is termed lime nitrogen or cyanamide of calcium. The second process consists in oxidizing atmospheric nitrogen by electrical means, and converting it into nitric acid, which is put into commerce as nitrate of lime with 13 per cent of nitrogen, which has the greater analogy with nitrate of soda and which like the latter is assimilable by plants. The two products come on the market as more or less dark dirty grey powders. Their percentage of nitrogen varies from 13 to 21 per cent. The following are the analyses given by Grandeau:—

TABLE LXXVIII.—ANALYSES OF CYANAMIDE (LIME NITROGEN AND NITROGEN LIME). (GRANDEAU.)

	Lime nitrogen.	*Nitrogen lime.*
Nitrogen	20-21	20
Calcium	40-42	45
Carbon	17-18	19·5
Chlorine	—	6·5

The only difference between the two products is that the nitrogen lime contains calcium chloride injurious to vegetation.

Manufacture of Cyanamide.—"Lime nitrogen" is manufactured in Italy by the Società generale per la Cianamide, the head office of which is in Rome in association with the Berliner Zyanid Gesellschaft. This company has acquired all the patents and processes relating to the manufacture of cyanamide of calcium and its derivatives. It afterwards assigned these patents for Italy and Austria-Hungary to the Società italiana per la fabricazione di Prodotti azotati, which has installed at Piano d'Orte a factory capable of producing 10,000 tons a year. It has just acquired at Almissa numerous waterfalls of a force of 50,000 H.P., which will enable it to manufacture 1,000,000 tons per annum. Manufacturing licences have been granted in France to the Société française des produits azotés at N.-D. of Briançon; to the Société Suisse near Martigny, and to the North-Western Cyanamide Co. near Odde in Norway, the head office of which is in London. A factory using a fall of water of 40,000 H.P. is in construction in America, and two others respectively of 2000 and 10,000 H.P. are in construction in Germany. The manufacture of cyanamide according to the first of these processes has just been modified by Polzenius, who adds 10 per cent of calcium chloride to the calcium carbide used so as to fix the nitrogen on the mixture at a much lower temperature [700° to 800° C. (1292° to 1472° F.)] than in the original Frank and Caro process of 2000° C. (3632° F.). The product so obtained is called "nitrogen lime" in opposition to the product "lime nitrogen" by the old process. But this distinction is one of pure form, for the two products have perceptibly the same composition. The nitrogen in these products costs 1·4 francs the kg. (say 6d. per lb.). The factory working this process is situated at Westerregeln in Germany. It is capable of producing 4000 tons of lime nitrogen per annum.

Manufacture of Nitrate of Lime.—As just mentioned, this process consists in oxidizing atmospheric nitrogen by electric means. In 1903, Prof. Birkeland of Christiania observed that the electrical discharges from the alternate current, at an average tension, dispersed in the magnetic field, which brought about the combustion of the nitrogen in the air. This process had the advantage over similar ones of requiring a much lower electric tension, say 5000 volts in place of 15,000, and to furnish much higher yields of nitric acid.

The air is burnt in an electrical oven having the form of a drum. This furnace was modified and improved by Samuel Eyde. In this drum the air is submitted to a temperature of 3000° C. By rapid cooling the nitrous oxide (NO) formed in the electric flame is retained almost entirely, whilst in former processes it was in great part lost. The nitrous oxide issuing from the furnace at a temperature of 600° to 700° C. (1112° to 1292° F.) combines with the oxygen to form NO_2, which is passed through a series of towers. It finally yields nitric acid of 50 per cent strength, which is saturated with lime. The mass is then heated to 450° C. (842° F.), which is its melting-point, then poured into cast-iron cylinders, where it solidifies slowly. In the beginning, crystallized nitrate of lime was manufactured which was difficult to use owing to its hygroscopic properties. This product melted between the fingers and could thus only be used mixed with peat dust. That was why they afterwards set themselves to make basic nitrate of lime; but this product only contains 11·7 per cent of nitrogen, which rendered its freight charges heavy, and formed an obstacle to its sale. Lately, the partially dehydrated salt tested 13 per cent of nitrogen. The first manufactory of any importance of this product was built at Notodden in Norway. The experience acquired in that factory has induced the management of the company to increase the plant, so as to make 8000 to 10,000 tons per annum. This factory is maintained by the Badische Anilin und Sodafabrik. The unit of nitrogen in nitrate of lime is sold at the same rate as the nitrogen in nitrate of soda.

Agricultural Experiments with Cyanamide.—Calcium cyanamide has of late years been the subject of numerous agricultural experiments by P. Strohmer, O. Botticher, Otto A. Stutzer and E. Wein.

It must be observed in a general way that calcium cyanamide neither suits humic acid soils (? peaty soils) nor light sandy soils. On the other hand, it may be used in all loamy soils of average fertility. Owing to the formation of dicyanamide, this manure ought to be spread at least eight days before sowing and covered in afterwards in not too superficial a manner. The action of cyanamide is weaker than nitrate of soda, it is also slower than the latter. But as the unit of nitrogen is supplied cheaper by the new manure a greater amount can be used to restore the balance. Without doubt cyanamide deserves attention. According to the experiments of Remy, this manure succeeds very well on clay soils, less so in sandy soils. F. Loehnis has observed that the conversion of cyanamide into ammonia in the soil is effected by bacteria, for example by the *B. Megatherium*, the *mycoid* and other species in part new. We know that the conversion of ammonia into nitrate is likewise effected by bacteria, and according to the researches of G.

Muntz and E. Laine, peat is an excellent means for bringing nitrifying bacteria to very great activity. For this purpose the peat is moistened with a solution of an ammoniacal salt after having mixed it with lime to fix the nitric acid formed. From very detailed comparative experiments by P. Wagner, B. Dorsch, S. Mals and M. Popp, "Land Versucht," 1907 (Vol. LXVI, p. 285), with cyanamide and various nitrogenous manures, it follows that :—

1. *Sulphate of Ammonia* and *Nitrate of Ammonia* have not shown great differences in their mode of action.

2. *Carbonate of Ammonia* produced in loamy soils exactly the same results as sulphate and nitrate of ammonia. In sandy soils it did not act normally on the culture in pots except at a dose of 0·75 grammes applied once ; stronger doses were injurious.

3. *Nitrate of Lime* acts normally up to the second dose (1·5 grammes) in loamy soil and up to the third dose in sandy soil (2·25 grammes). But from that moment there is an injurious action, especially in loamy soils. The high percentage of basic nitrate of lime and the still higher percentage of nitrate of lime produce injurious effects.

4. *Cyanamide* in a dose of 0·75 grm. once applied has given a favourable result in pots, although a little less than other nitrogenous manures of equal dose.

5. *Fish Guano* produced an average useful effect of 78, the action of nitrate of ammonia and of sulphate of ammonia being supposed to equal 100.

6. *Green Manures* have produced on sandy ground the same useful effect as fish guano in loamy soils ; they were slightly less effective.

7. *Nitrate of Soda, Chili Saltpetre* and *Sulphate of Ammonia* have regularly produced higher yields and a better utilization of the nitrogen than cyanamide.

The general result of all these agricultural experiments is the following :—

If the value of nitric nitrogen be expressed by 100, the value of the nitrogen in cyanamide is represented by 90. The lime nitrogen acts a little more feebly when its decomposition in the soil gives rise to the formation of dicyanamide resulting from the action of carbonic acid, humic acid, heat and the absence of bacteria. The factors which favour the action of cyanamide are uniform distribution (fifteen days before the time of sowing), perfect mixing of the manure with the soil, sufficient moisture to the soil, a loamy soil rich in bacteria, spreading at the latest on 15th February for winter plants.

Rules for the use of Cyanamide.—Immendorf has drawn up the following rules for the use of cyanamide :—

1. Cyanamide does not suit humic acid soils, where its action is uncertain and where it may poison plants.

2. For the same reason its use is not recommended in light sandy, somewhat torpid soils, especially those with an acid reaction.

3. All other soils, especially loose friable soils, which contain enough lime and are regularly manured with farmyard dung, may be manured with cyanamide.

This new manure may be successfully applied bearing in mind the following observations :—

(*a*) The dose to use per hectare to be from 150 to 300 kg. (330 to 660 lb., say 132 to 264 lb. per acre), equal to 30 to 60 kg. (66 to 132 lb.) of nitrogen per hectare (say 26·5 to 53·8 lb. per acre), according to the fertility of the soil.

(*b*) As the cyanamide gives off an enormous amount of dust which is possibly the most unpleasant defect of this manure, the best thing to do, if a manure distributor be not available, is to mix it intimately with double its weight of not too moist soil and to spread it immediately.

(*c*) The spreading of the manure ought to be done eight to fifteen days before sowing, according to Frank. However, when this manure is applied to soils which suit it, this delay is not to be insisted on (unless in case of too great drought); if it be spread three to four days before sowing and suitably covered in, cyanamide completely loses its properties injurious to the germination of the seed.

(*d*) It is essential to mix the manure with the surface layer of soil immediately after distribution, covering it in with the plough. Care should be taken not to spread the manure so long as the surface of the soil is humid and very hot.

(*e*) In no case should cyanamide be used as a top-dressing, at least until after the crop has been removed, for in that case it would be more injurious than useful.

Drawbacks in the Use of Nitrate of Lime.—A. Pitzewitz has communicated to the German Agricultural Society the results of experiments which he made this year with nitrate of lime as manure.

"I used," he says, "in the spring of this year large quantities of nitrate of lime as much on grain crops as on beets, and I can say that from the point of view of the results, nitrate of lime has not shown itself inferior to nitrate of soda.

"Nevertheless, I will take care not to use it again, for the following reasons :—

"1. Stored for a long time in casks nitrate of lime suffers considerable loss in weight. Having left the casks from January in dry warehouses, I found at the time of spreading in April-May, 1898, an average loss by volatilization of 20 to 25 lb. per cask.

"2. It is very difficult to regulate its distribution by the drill. Nitrate of lime, moreover, has the grave drawback of enveloping the

persons about, or following the machine as well as the horses, in a layer of tacky dust, so that labourers refuse to apply it. It is therefore for that reason that it is impossible to spread nitrate of lime by hand, for the hands would be injured, and the wind projecting the nitrate of lime about the body would endanger the eyesight. It is therefore necessary (1) to find a manure distributor which will obviate these drawbacks; (2) to improve the conditions of preserving the product during storage."

To obviate the deliquescent properties of nitrate of lime, it is mixed with equivalent quantities of alkaline sulphates, sulphate of potash or magnesia, or calcined kieserite. The product so formed is not more deliquescent than nitrate of soda, and forms a dry powder.

N.B.—The author, following French custom, uses in the text the term *chaux azote*, "lime nitrogen," for cyanamide almost throughout, but such a term is too vague and misleading. It has been altered to the more intelligible trade term. Attempts to differentiate the separate products of mere variation in manufacture in such a vague way as ringing the changes on the precedence and sequence of the two main ingredients, can only create confusion where everything is plain sailing. If a distinction were at all required, α and β cyanamide ought to have been chosen. Such distinctions are as ridiculous as "nitrogen sulphate" and "sulphate nitrogen" would be for sulphate of ammonia from bones and from coal respectively.

CHAPTER XV.

NITROGENIZED PHOSPHATIC MANURES.

Concentrated manures containing both nitrogen and phosphoric acid in important quantities are only represented on the market under well-determined forms. Such manures have played a very important rôle in the history of agriculture. They were the starting point of chemical manures, and it is through them that we first learned to fertilize the soil and to increase the vegetable production, otherwise than by farmyard manure. It was only afterwards that agriculture came to the large series of phosphates, potash salts and nitrogenous matter which have to-day become the indispensable factors of all rural exploitation. These manures are Peruvian guano and bones, to which had to be added gradually the different manures composed from waste of animal origin described in the preceding chapters.

Peruvian Guano. — Its Composition. — Like phospho-guanos already described, Peruvian guano is essentially a product of the decomposition of the excrements of sea-fowl. It has an analogous origin, but is formed in a different manner; whilst Baker guano scarcely contains 1 per cent of nitrogen with about 80 per cent of phosphate of lime, Peruvian guano has preserved almost integrally throughout centuries the nitrogenized organic matter, owing to the climatic conditions which supervene in the countries where such deposits are found. Birds' excrement (pigeons' and hens' dung) has been known for a long time as a valuable manure; it is distinguished by great richness in nitrogen, contrary to what occurs in the case of mammals. But the excrements of birds of prey (carnivoræ) are particularly rich in nitrogen, and the sea-birds which produce guano fall exactly into this category; whilst in fact the dried mixture of the solid and liquid dejections of man contain on an average 10·45 per cent of nitrogen and 3·88 per cent of phosphoric acid, the dried dung of the eagle contains 35·7 to 37·7 of nitrogen and 0·32 to 3·99 of phosphoric acid. This explains why the guano of sea-birds is very rich in nitrogen, whilst the urine of these birds, instead of being liquid like that of mammals, is thick, and thus does not penetrate into the soil.

The deposits of nitrogenized guano extend over a vast surface of the West Coast of South America, its quality always varying

according to the situation of the different deposits. The most esteemed kind was that formerly collected on the Chincha Isles, well known to the ancient Peruvians, who came there to search for manure to fertilize their wheat and potato fields. But these islands are now completely exhausted, as well as those of Ballestas, Guanape and Macabi. It is, therefore, unnecessary to describe them. However, we cannot help quoting the analyses of the samples of guano brought from these islands by Alexander de Humboldt in 1804, and of some others because they correspond near enough with the guanos now imported from these countries (see p. 280). The following are some of the distinctive characters of Peruvian guano, according to J. Girardin :—

It is a dry powder of a pale yellow or *café au lait* colour, but it becomes chocolate as it ages or when it is exposed to the air; it absorbs, moreover, in the latter case much moisture, becomes heavier and sticks to the fingers. It exhales a strong putrid or ammoniacal odour which induces sneezing. It has a very sharp salt taste. It shows in bulk numerous whitish semi-hard concretions which can be crushed between the fingers, and which when exposed to the air soon slake and fall to dust exhaling a very strong ammoniacal odour. Thrown into water, Peruvian guano soon finds the bottom and lets nothing rise; when heated it blackens, burning with a feeble flame with production of a strong ammoniacal vapour; the residue which it leaves is in the form of a white slightly bluish cavernous slag; the weight of this residue only varies between very near limits, 27·5 to 35 per cent.

Triturated with powdered quicklime, Peruvian guano immediately gives off a strong ammoniacal odour. When thrown into a glass containing a concentrated solution of chloride of lime, it soon gives rise to disengagement of bubbles of gas which continue for a somewhat long time. In contact with hydrochloric acid, it only produces a slight effervescence; moistened with nitric acid and dried in a porcelain capsule, it assumes a fine red colour. Finally, this guano only rarely contains silicious pebbles, and it contains only 1 to 1·5 per cent of sand; the maximum is 2·5 to 3 per cent.

In this same report Girardin gives the analyses of thirteen samples taken by himself on board ship on their arrival in Havre. This document is so interesting that it will be useful to reproduce it here. The guanos delivered, afterwards were less rich in nitrogen and more rich in phosphoric acid than those which gave the old analyses. That is not surprising, and each new sample yields different results; for on the one hand the workmen entrusted with collecting it are not careful enough, on the other hand the deposits are continually altering under the influence of moisture, however small the rainfall in these countries. But the chemical transformation of the guano is not the same in all the parts of a deposit.

TABLE LXXIX.—ANALYSES OF PERUVIAN GUANO.

Composition.	According to	
	Vauquelin and Fourcroy. Per cent.	Klaproth. Per cent.
Urate of ammonia	9·0	16·0
Oxalate of ammonia	10·6	—
„ lime	7·0	12·75
Phosphate of ammonia	6·0	—
Double phosphate of ammonia and magnesia	2·6	—
Sulphate of potash	5·5	—
„ soda	3·3	—
Sodium chloride (common salt)	—	0·50
Ammonium chloride	4·2	—
Phosphate of lime	14·3	10·00
Clay, sand, etc.	4·7	32·00
Water and organic matter	32·8	28·75
	100·00	100·00

TABLE LXXX.—ANALYSES OF PERUVIAN GUANO.

	Dark Yellow Guano (Oellacher).	Guano from Liverpool (Bartel).	Lima Guano (Voelcker).
Urate of ammonia	12·20	3·444	1·0
Oxalate of ammonia	17·73	13·351	10·6
„ lime	1·70	16·360	7·0
Phosphate of ammonia	6·90	6·250	6·0
Double phosphate of ammonia and magnesia	11·63	4·196	2·6
Sulphate of potash	4·00	4·227	5·5
„ soda	4·92	1·119	3·8
Common salt	0·40	0·100	—
Ammonium chloride	2·25	6·500	4·2
Phosphate of lime	20·16	9·940	14·3
Carbonate of ammonia	0·80	—	—
Humate of ammonia	1·06	—	—
Phosphate of soda	—	5·291	—
Carbonate of lime	1·65	0·600	—
Waxy matter	0·75	5·904	—
Sand and clay	1·68		—
Water	4·31	22·718	4·7
Organic matter and undetermined	8·26		32·3
	99·40	100·000	92·0

Thus, leaving out of account the superficial lamellary layer which obviously contains the most recently formed guano, a layer the stratifications of which may be compared to the annual rings formed in the trunk of a tree, three superimposed layers may be distinguished in the deposit—the superficial brown layer, the middle yellow layer, and the lower brown layer. The richest guano is that of the middle layer. That of the upper and lower beds is the poorest. This fact is easily explained by considering the incessant phenomena incidental to the formation of these kind of deposits.

TABLE LXXXI.—ANALYSES OF PERUVIAN GUANO.

	1	2	3	4	5	6
Water . . .	8·990	20·054	17·160	20·300	11·100	17·520
Sand and pebbles .	1·2000	1·250	1·000	1·190	10·400	15·400
Phosphate of lime .	24·000	24·000	24·500	28·000	25·500	37·000
Other insoluble salts .	2·6000	3·000	0·500	2·700	20·700	11·238
Potash . . .	0·9648	2·319	2·894	1·061	2·180	2·162
Other soluble salts .	5·0352	2·981	4·306	0·239	0·92	1·380
Organic matter and ammoniacal salts .	57·2100	46·396	49·640	46·510	29·00	15·300
	100·0000	100·000	100·000	100·000	100·000	100·000
Nitrogen per cent .	11·30	12·18	13·47	14·58	11·30	2·66
Ammonia ,, .	4·90	8·230	7·04	4·90	2·29	2·30

TABLE LXXXII.—ANALYSES OF PERUVIAN GUANO.

	7	8	9	10	11	12	13
Water . . .	18·800	12·740	15·025	19·740	21·500	15·300	18·00
Sand and pebbles .	4·300	3·710	2·245	2·280	17·700	20·000	16·00
Phosphate of lime .	40·300	18·000	31·800	34·800	35·600	11·500	33·800
Other insoluble salts	5·800	38·200	25·200	23·200	1·100	18·350	12·300
Potash . . .	2·026	0·771	0·578	1·824	2·500	0·676	0·4824
Other soluble salts .	10·974	14·329	13·622	8·576	0·300	2·874	8·8176
Organic matter and ammoniacal salts .	18·100	12·250	11·530	9·580	21·300	31·300	10·600
	100·000	100·000	100·000	100·000	100·000	100·000	100·0000
Nitrogen per cent .	4·48	1·28	1·82	1·09	4·82	4·12	1·250
Ammonia ,, .	1·416	0·183	0·183	0·176	0·76	traces	traces

Although rain is very rare in these countries, the surface of the deposit is none the less moistened in a more or less constant manner by the mists and fogs of winter. Now, moisture by its

presence alone diminishes the value of the guano of the superficial bed, besides it dissolves salts of potash, ammonia, lime and magnesia in so far as they are soluble and causes them to pass into the middle bed. To this downward transition there is a corresponding ascending transition from the lower beds. In fact the guano of the lower bed in contact with the soil is in a state of incessant decomposition, and gives off ammonia and carbonate of ammonia, which being very volatile ascend towards the top. The two opposite currents meet in the middle zone. The dissolved earthy salts fix the ammonia, which is thus converted into stable compounds. It is, therefore, easy to understand that the middle bed ought to be the richest in nitrogen, especially in ammoniacal salts. If this transfer of matter in itself sufficiently explains the great differences in composition revealed by analysis, it is not the sole cause. Peruvian guano does not wholly consist of the excrement of sea-fowl. Remains of seals and other marine animals are found in the lower beds in a state of curious preservation. It is, therefore, right to admit that these islands at a previous epoch when they were lower, served as a refuge to a great number of these animals, and that after they had become inaccessible owing to their volcanic upheaval they were the home of sea-fowl. This hypothesis enables us to understand why the brown guano of the lower bed is of less value; for the flesh and the decomposed bones of which it consists are less rich in nitrogen than the birds' excrement. The composition of guano, therefore, varies according to whether it comes from the upper, the middle, or the lower bed of the deposit. The concretions (nodules) of the upper bed have a composition identical with that of the powder in which they are embedded. Their colour and their structure enable one at first sight to recognize the guano from the surface bed. The nuts of guano from the middle bed are distinguished from the surrounding mass by their colour, which is paler, sometimes almost white, and they contain a crystalline nucleus or have a crystalline structure here and there. They consist chiefly of ammoniacal salts, oxalate and carbonate, and consequently contain more nitrogen than the guano in which they are embedded. The difference is as much as about 1·5 per cent, and much more in the case of very pure pieces. The nodules, the analyses of which are given here, according to Karmrodt and Phipson, come undoubtedly from the middle bed. They contain :—

TABLE LXXXIII.—ANALYSES OF GUANO FROM MIDDLE BED OF PERUVIAN GUANO DEPOSITS.

	Karmrodt. *Per cent.*	*Phipson.* *Per cent.*
Oxalate of ammonia	41·28	—
Carbonate of ammonia	—	76·93
Urate of ammonia	4·09	—
Alkaline urates	—	1·09
Nitrogenized organic matter	10·17	—
Phosphate of potash	9·52	—
,, soda	9·08	—
,, ammonia	7·57	—
,, lime (monacid)	—	1·14
Carbonate of lime	—	9·91
Sulphate of potash	7·49	traces
,, lime	3·40	traces
Magnesia and chlorine	—	traces
Moisture	7·40	10·93
	100·00	100·00

The lower beds of the deposit consist chiefly of salts of the alkaline earths, and the aggregations which are met with have also the same composition. It is sulphate of potash which predominates in the nodules of these beds. The following is the analysis of one of these nodules, according to Kraut:—

TABLE LXXXIV.—ANALYSIS OF PERUVIAN GUANO NODULES (LOWER BED).

	Per cent.
Sulphate of potash	45·64
,, soda	13·22
,, ammonia	10·23
Oxalate of ammonia	9·14
Phosphate of ammonia (basic)	12·09
,, ,, (monacid)	4·78
Organic matter	0·94
Insoluble	1·90
Water	2·06
	100·00

As observed above, the percentage of nitrogen in Peruvian guano varies between 3·76 and 9·34, it is therefore much lower than about 1860. The Chincha islands deposits have a composition somewhat like those of the old guano, as the following analyses of the Halle experimental station show.

The guano of different cargoes contained (see Table LXXXV, p. 284). As will be seen further on, guano is no longer sold except in the dissolved state. As guano, leaving its nitrogen out of account, consists mainly of phosphoric acid, in the form of phosphate of lime, it is, most generally, insoluble in the crude state. In certain very

favourable circumstances, rarely met with, it becomes soluble in the soil, owing to the nitrogenous matter with which it is mixed. But beyond these conditions, it is no more soluble than the guano from Baker's Island, and consequently it is inactive; it is no longer sold except in the soluble condition.

TABLE LXXXV.—ANALYSES OF DIFFERENT CARGOES OF PERUVIAN GUANO.

	I. Per cent.	II. Per cent.	III. Per cent.	IV. Per cent.	V. Per cent.	VI. Per cent.
Phosphoric acid, total	8·70	11·40	9·0	9·25	8·65	10·30
Phosphoric acid soluble in water	2·65	4·25	2·15	2·40	2·55	5·25
Phosphoric acid soluble in citrate, after Petermann	4·60 (7·25)	3·70 (7·95)	4·60 (6·75)	4·90 (7·30)	4·70 (7·25)	1·80 (7·05)
Nitrogen, total	8·20	13·35	14·60	8·90	8·85	8·60
,, ammoniacal	1·95	3·05	1·85	2·40	2·65	7·20
Nitrogen, nitric	0·00	0·05	0·00	0·10	0·10	0·05
,, organic	6·25	10·25	12·75	6·40	6·10	1·35
Potash	2·10	3·05	2·45	1·95	2·30	4·25
Of total phosphoric acid, soluble in water and citrate, per cent	83·33	69·7	75·0	79·0	83·0	68·4

Dissolved Peruvian Guano.—Under this designation the Anglo-Continental Co. deliver a special sort of guano with a guaranteed percentage of 7 per cent of nitrogen, 9·5 per cent of phosphoric acid soluble in water (= 10 to 11 per cent of total phosphoric acid), and 1 to 2 per cent of potash (= 2 to 3·5 of sulphate of potash). As guano is generally loaded into ships in the bottom of the hold as ballast, a part of the cargo is perforce drenched with sea water. In the early days, importers placed this damaged portion on one side; but it ended in locking up considerable capital, and means had to be taken to unlock it. Attempts were made to dry the damaged guano and to sell it cheap to farmers. But this method of utilizing damaged guanos had numerous drawbacks. Nothing in fact could distinguish it from the guano which had not been drenched, neither the outside appearance nor the smell, nor the chemical analysis itself, which showed the same percentage of nitrogen as normal guano.

The importers carefully considered these drawbacks. Accordingly, acting on the advice of the chemists, they attempted to improve the damaged guano by dissolving it with sulphuric acid. As the manure so treated gave good results, the result was that this

treatment was applied to all guanos indifferently, so that for the past fifteen years, 96 to 97 per cent of the dissolved guanos was produced from non-deteriorated guano. In the later contracts between the Peruvian Government and the Peruvian Guano Co., this state of things has undergone no alteration. The process used to dissolve Peruvian guano is as follows :—

As the guano exists in big lumps in the raw state it must first of all be ground to a fine powder. As it would be idle to pass all the mass of guano through the crusher, the latter is combined with a shaking sieve to separate the powder from the big lumps, which are alone ground.[1] The crusher also eliminates from the guano stones (granite) brought from the deposits, which when they are not too large are fixed between the bars of the machine, from which they may be removed. In this way about 1 per cent of stones is obtained, which is debited against the supplies of the guano at the purchase price.

The powdered guano thus obtained is then mixed with 22 per cent of its weight of sulphuric acid of 66° B., sp. gr. 1·84 (168° Tw.), or with the equivalent of the acid at 60° B. As the phosphoric acid exists as dibasic phosphate, the solution requires no plant, and is done by simple shovelling. The material is then laid in heaps, where it solidifies. When the reaction is finished, the guano is again passed through the crusher to reduce it to powder, the form under which it is put on the market. Dissolved guano contains 5 to 7 per cent of nitrogen and about 10 per cent of soluble phosphoric acid ; it is sold with a guaranteed analysis.[2]

As the Anglo-Continental Guano Co. can only supply a product of uniform analysis, by carefully sorting and mixing the raw guanos and not by the addition of foreign matters, sulphate of ammonia, etc., it follows that the constant decrease in this nitrogen content of the raw guanos reacts also on that of the dissolved guano. Since 1878 the guano has been delivered uniformly with 10 per cent of phosphoric acid and 5 to 7 per cent of nitrogen, at the wish of the buyer. Dissolved guano has a considerable advantage over raw guano—that of acting with absolute certainty. If the phosphoric acid of raw guano dissolve in the soil, when the temperature conditions lend themselves thereto, it is precisely this subordination which lessens its value and renders it illusory. As the solubility

[1] The author seems to the translator throughout the manufacturing section to have recourse to the disintegrator a little too often when it seems possible less drastic means would do. But here the author himself owns the futility of grinding powder, but throughout the previous text he seems to recommend passing everything through the disintegrator—the whole manure such as it is, not only core but the friable portion as well and even loose friable superphosphate.—Tr.

[2] All manures in Great Britain must be so sold to meet the requirements of the Fertilizers Act.—Tr.

of the phosphoric acid, moreover, depends on the percentage of alkaline salts in the guano, present-day raw guanos are much less soluble than the old Chincha guanos. Farmers were, therefore, justified up to a certain point in attributing to the old guanos now exhausted a characteristic specific action, not only because these guanos contained 12 per cent of nitrogen against 7 per cent in the present products, but also because the ammoniacal salts present are insufficient to bring the phosphoric acid to a soluble condition in the soil.

By now using 100 lb. of raw guano with 7 per cent of nitrogen and 14 per cent of phosphoric acid, the same results would be obtained as formerly with 58 lb. of the old guano (containing 12 per cent of nitrogen and 12 per cent of phosphoric acid), mixed with 20 lb. of 36 per cent phosphoric acid and bone ash. It follows that the use of raw guano in these circumstances would be sheer waste of phosphoric acid. Taking it for granted that all the phosphoric acid of the old guano was soluble in the soil (which is not absolutely demonstrated), it may be asserted with certainty that only the half of the phosphoric acid is soluble in the guano of the present day. Now by dissolving the guano the farmer can utilize all the phosphoric acid present in the manure. Another advantage which dissolved guano has over raw guano, is that its nitrogen cannot be volatilized nor consequently lose its nitrogen in the air. All the carbonate of ammonia is converted into sulphate, and if new portions could be formed it would at once be fixed by the sulphuric acid.

Finally, dissolved guano is more easily applied than raw guano; it contains neither lumps, which oblige the farmer to crush it, nor dry powder, which, spread in stormy weather, lost itself in the neighbouring field. Dissolved guano is in the form of a moist but not tacky powder. The farmer has so well understood these advantages, that he has given up the use of raw guano.[1]

[1] The farmer has no option but to give up what is not available. When the old guano was applied to grain crops at the time of sowing it was applied broadcast, and in the north-east of Scotland by an experienced man who distributed it with both hands, swinging them rhythmically, and alternately throwing to the left with his right hand and to the right with his left hand, in a manner to be seen to be appreciated. If these farmers could get the old guano back again they would soon find means of applying it. In former days the bags were distributed over the field, and the requisite amount carried by women on their heads, in a wide sieve-shaped vessel with a leather bottom, to the man sowing it, the whole forming a picturesque scene when the man distributing the manure had the knack of swinging his two hands almost simultaneously and in opposite direction. Grain was sown in the same way. If the guano burned the clothes and got in the eyes that only showed its virtue. Now the farmer only gets the dead body, whose spirit, volatile ammonia, has departed. The sulphuric acid has killed it by fixing it, even if it has dissolved the phosphates; besides it must be remembered that the sulphuric acid used to dissolve it only costs £2 per ton at the most, and that the cost of the guano to the concessionaires is diminished *pro rata*.—Tr.

Other Nitrogenized Guanos. — Amongst other nitrogenized guanos, mention must be made of Ichaboe guano (Ichaboe is an island on the West Coast of Africa). This manure has been known for a long time, but was never of very great commercial importance, because the first arrivals only contained 8 per cent of nitrogen and 20 per cent of phosphoric acid; those which followed tested less and less. Ichaboe guano rather approaches phospho guanos. Latterly new deposits of guano have been found on the island of Ichaboe, formed by sea-fowl, and not damaged by moisture. The percentage of nitrogen in this guano, which contains feathers and the undecomposed carcases of birds, rises to 14·4 per cent, and its phosphoric acid content to 17·6 per cent.

Different deposits of guano were discovered a long time ago on different points of the African coast, such as those of Algoa Bay, Saldanha, and those of Cape Colony. But these deposits, almost all exhausted by moisture, never had a great importance.

Seal Guano.—Seal guano has been found in several parts of the West Coast of South America, in the Bay of Ferrol, in the Lobos Isles, and in the Isle of Tortuga. These deposits are even now the habitat of seals, so that they are incessantly being formed. In the Lobos Isles, the guano forms a bed 70 metres (say 230 feet) thick at many points; it consists chiefly of the carcases of animals, bones, fur, hair, etc., all slightly soluble substances. This guano contains much less nitrogen than true Peruvian guano; it is analogous to the guanos of the lower bed of the Chinchas deposits above mentioned.

Bat Guano.—There was formerly on the market a guano of this kind, under the name of Sarde guano. Stockhardt found in that product:—

TABLE LXXXVI.—ANALYSIS OF BAT GUANO.

	Per cent.
Nitrogen	2·05
Phosphate of lime	35·30
Alkaline salts	3·60

It consists chiefly of bat excrements mingled with the dead bodies of these animals. Bat guano is found in grottoes and rock fissures, on the shores of the Mediterranean, in Brazil, Hungary, France, near Vesoul in Egypt. The largest deposit up to now is that of Kolumbacz, on the Danube, which contains 4000 tons of guano.

Hungarian Bat Guano contains, according to Scheibler, 1·88 per cent of nitrogen and 11·64 per cent of insoluble phosphoric acid; it is only, therefore, of small value. The guano found in the

neighbourhood of Cracow is richer. It forms a brown mixture of excrements and bone debris. Analysed by Krocker, it gave :—

TABLE LXXXVII.—ANALYSIS OF HUNGARIAN BAT GUANO.

	Per cent.
Moisture	7·50
Combustible matter	75·20
Ash	17·20

Its total nitrogen content is from 9·170 per cent, of which 3·60 per cent is as ammoniacal salts, 0·118 per cent as nitric nitrogen, and 5·452 as urea, and other organic bodies. The ash consists in part of phosphate of lime, in so far that the phosphoric acid content is 3·825 per cent.

Egyptian Bat Guano contains, according to Popp :—

TABLE LXXXVIII.—ANALYSIS OF EGYPTIAN BAT GUANO.

	Per cent.	
Urea	77·800	Average of 37 analyses : nitrogen 37 per cent (soluble phosphoric acid 7·18 per cent).
Uric acid	1·250	
Creatine	2·550	
Phosphate of soda (monacid)	13·450	
Insoluble	0·575	
Moisture	3·660	
	99·285	

This guano is not only the richest in nitrogen of all guanos found up to now, but moreover of all nitrogenized manures.

Eboli Bat Guano (province of Salerno) contains, according to Dr. G. Paris, 2·996 per cent nitrogen, chiefly nitric nitrogen. There is also found :—

TABLE LXXXIX.—ANALYSIS OF EBOLI BAT GUANO.

	Per cent.
Moisture	18·20
Organic matter	29·11
Ash	52·87
	100·18

The ash contains 20·69 per cent of phosphoric acid, of which 47·96 per cent is soluble in citrate. All these deposits are comparatively unimportant.

Conclusion.—Fifty years ago Peruvian guano completely dominated the manure market; no other artificial manure could at this epoch meet the wants of the farmer.[1] Nitrate of soda was too

[1] The old raw Peruvian guano was exceptionally highly esteemed by the farmers in Scotland, where the translator has also seen it in bags branded "ammonia fixed" in the early 'sixties. The raw guano suited the soil and climate of the Moray Firth coast better than any other manure.—Tr.

high in price, the manufacture of sulphate of ammonia was in its infancy, that of superphosphates was just commencing and could only maintain itself with a great struggle in presence of guano; the preparation of bone manures, although well advanced at the time, was limited in its scope by the poverty of the raw material. Under these conditions, Peruvian guano was the sole regulator of the price of nitrogen and of phosphoric acid on the international market.

To-day the situation is not the same. The improvement in the condition of manufacture in the nitrate districts enables the concessionaires to flood the European markets at prices which formerly would have been regarded as ridiculous. The production of sulphate of ammonia in gasworks pursues an ever-increasing progress. The exploration of the Pacific Ocean is always discovering new islands of phosphatic guano. Enormous deposits of phosphates have been discovered. Finally, blast furnaces furnish the farmer with large quantities of phosphoric acid in basic slag. The 2 or 3 per cent of potash supplied by Peruvian guano is largely replaced by Stassfurt salts, Aschersleben salts, etc. This abundance of manure is very reassuring as regards the future, and the near exhaustion of the phosphatic guanos may be regarded without apprehension.

But it is not so as regards nitrogen, which only forms a part of guano. For however important may be the resources of the farmer from this point of view, and although he now only utilizes human excreta to a slight extent, nitrogenous manures are none the less the dearest. The discovery of Hellriegel of plants capable of fixing atmospheric nitrogen through the intervention of certain bacteria, now enables the farmer to economize on nitrogenous manure. Rumpler quotes a rural farm which collects 40 tons of beets to the hectare (16 tons to the acre) with a very high percentage of sugar, and using only a small amount of nitrate, by ploughing in green manures [vetches (tares)] and completing them by a strong application of superphosphate. Green manuring completed by a good dose of phosphoric acid, potash and lime, forms the manure of the future. It is likely to revolutionize all the present-day systems of farming by freeing the farmer from paying tribute to exotic nitrogen. In any case it holds the key to the solution of the exhaustion of guano question.

Fish Guano.—Historical Review.—The sea is an inexhaustible store of fertilizing matter. Independent of its own richness, it is incessantly receiving organic and mineral matter removed from the soil or detached from the mountains by the rain of storms. Moreover, it receives the human excreta which civilized towns run into the rivers. All these materials contribute to maintain the marvellous fertility of the sea. For many years the sardine fishing has

been a highly important source of profit to the inhabitants of the Brittany coast, and has powerfully contributed to maintain a sailor's nursery. As far back as 1620, in the single small village of Port Louis, 4000 barrels of sardines were packed annually. Up to 1823 the only method of preserving sardines consisted in salting them and pressing them in barrels; they were thus put on the market under the name of "pressed sardines". This method of preservation was replaced in 1824 by a new process known under the name of Ampère [? Appert], its author. This process consists in removing the head and the viscera from the sardines, and to pack the latter in tinned iron boxes, in which they are preserved in oil after having undergone a preparation known to everybody nowadays. This new method produced much waste of considerable fertilizing value for the soil. However, this debris was not utilized; in the beginning it was run into the sea, where it was lost without any profit. It was only in 1847 that Demolon conceived the idea of utilizing it as a manure. He desired first of all to use it in the raw state, but as he received it at a time when the crops had been already laid down, he was obliged to store it for a certain time. It then putrefied and became a pest to the neighbourhood. Demolon then tried to store it by a more efficacious and less annoying process. After having tried different means he conceived the idea of boiling it. In that way he succeeded in extracting the oil, then he dried it and reduced it into cakes which kept as well as oil cakes. In 1850 he built a factory in Newfoundland to treat there the debris left from the cod-fishing. The plant of this factory consisted of six boilers to boil the fish, sixty presses, two graters and four mills. The whole was driven by four small steam engines. The fish as it came to the factory was fed into a revolving horizontal steam-jacketed pan. The steam entered through the centre of this pan, heated the double jacket, and in ten minutes the fish was cooked. The door of the pan was then opened and the fish fell on to an inclined plane. The water and oil fell into a reservoir, and the solid parts were pressed, enclosed in *scourtins* analogous to those used for the extraction of olive oil. The products were afterwards dried in a stove with a superficies of 900 metres (say 3000 ft.). Finally, the oil was run into a sufficient number of vats. When the fish debris was boiled, pressed and grated, it was placed on frames lined with cloth which pushed each other through the stove, so that after half an hour the completely dried debris fell into a hopper and thence into mills in which it was pulverized. Without boiling the fish it could never be dried completely or the oil extracted. By boiling, the oil was extracted, which sufficed to pay all the costs. This manure contained 5 per cent nitrogen and 49 per cent phosphate, and was sold at 30 francs

the 100 kg. (12s. a cwt., £12 a ton). But this new industry injured too many interests. Demolon and his partner were circumvented by speculators, who, once masters of the factory, found nothing more urgent to do than to demolish it. Demolon's idea was not long in being taken up again in Norway, where fish manure was made after the same process, then in America, especially at Boston, and in Great Britain, always according to Demolon's process. Jules Loreau & Co. have built at Kernevel, near Lorient, that is at the door of the sardine factories (sardines à l'huile), so numerous in these districts, a factory where they convert into manure all the detritus coming from these factories. This debris, which consists largely of heads, cartilages and intestines, is received at the factory on tables or sloped floors which allow the brine charged with blood to drop into a pit, whence it is afterwards drawn off by a pump; there is thus a liquid and a solid portion. The liquid portion, that is the brine mixed with a certain quantity of oil which is separated to be sold, is delivered to the local farmers, who utilize it to enrich their farmyard dung and especially for fertilizing meadows. A proportion of ten to fifteen barrels to the hectare (say four to six barrels to the acre) is sufficient to produce very good crops. This manure undergoes an ammoniacal fermentation in the pit and its action on vegetation is most energetic; it should therefore only be used on moist ground, as after rain, for example; on analysis it shows a proportion of 1·34 per cent of nitrogen. The fish debris after draining is lifted, made into a heap and boiled over a naked fire, when a little water is added and clear brine; the boiling lasts two hours for 400 kg. (880 lb.) of sardine heads. After boiling, the material is piled in layers between two wrought-iron plates and submitted for five hours to the action of a press, from which it issues in the form of a cake. The 400 kg. (880 lb.) yield on an average 100 kg. (220 lb.) of cake with 25 per cent of water. This cake is air-dried and then pulverized in a flatstone mill, whence it issues ready to be delivered to the farmer. A pair of flatstone mills yield 1 ton to 1½ tons of ground cake in twelve hours, according as the weather is more or less dry. The average composition of this manure is the following:—

TABLE XC.—ANALYSIS OF BRITTANY FISH GUANO.

	Water		5·00
Volatile matter	Organic matter	50·50	57·00
	Nitrogen	6·50	
Ash	Phosphate of lime	28·00	38·00
	Carbonate of lime and (alkaline) salts	5·50	
	Silica	4·50	
			100·00

This fish manure, which is in great part delivered to the farmer as it is, is also used at Kernevel in the manufacture of compound manures and in that of phospho guano. The chief compound manure, which is sold under the name of *Breton Manure*, is merely fish cake mixed with a sort of fucus (seaweed) extracted at low water. As to the phospho guano, it is manufactured by treating the crushed fish cake with sulphuric acid of 50° B. Next morning it forms a paste and ends by drying. It is advantageously used for different crops, particularly for beets. It contains on an average 2·5 of nitrogen. In Brittany the sardine industry commences at Croisic and ends at Douarnenez; it yields about 6000 barrels of sardine heads; a barrel of 225 litres contains on an average 30,000 heads.

Manufacture of Fish Guano in Norway.—At the present day fish guano is manufactured chiefly in Newfoundland and on the islands of the Norwegian coasts. The most important factories of this manure are in the Lofoten Isles to the north of Bergen. The fishing industry, which is very important in the North Sea, and the flesh of which is sold under the name of cod, yields a very abundant raw material; the head, the fins, the intestines, etc., are utilized. Norwegian fish guano perceptibly resembles steamed bone dust, although it does not occur in the same pulverulent form as the latter. The process generally used is the same as that for making bone dust. The fish debris is steamed, dried, and ground; steaming presents certain difficulties. When the digester described on page 264 is used, the material cakes so that the steam cannot pass through it; steaming is therefore too strong on the edges and the material is too much degelatinized, whilst the centre escapes steaming. To remedy this drawback, the firm of M. Friedrich of Plagwitz, near Leipzig, has built a horizontal digester, an interior perforated cylinder revolving around an exterior cylinder. The material to be treated is fed into the interior cylinder; it is heated by steam which is injected into the exterior cylinder; then a rotary motion is imparted to the first, the effect of which is to turn the material over unceasingly and to renew the surfaces in contact with the steam. The gelatinous solution is separated through a tap at the bottom of the apparatus, and it is evaporated to transform it into solid gelatine. After cooking, the material contains a rather large proportion of water. That is why the material is dehydrated before passing it to the drying machine by passing it through either a hydraulic press or a centrifugal machine. A greasy liquor is thus obtained which separates a little oil on standing. The dry material is crushed in the same way as bones. For some years back fish guano has been treated by sulphuric acid. It contains on an average 7·9 per cent of nitrogen and 12 to 16 per cent of phosphoric acid. The following are the analyses of several Norwegian guanos:—

TABLE XCI.—ANALYSES OF NORWEGIAN FISH GUANO.

	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Water	12·30	18·44	13·02	10·54	8·65
Organic matter . . .	53·70	70·80	49·40	50·92	59·15
Nitrogen	8·15	8·15	10·38	6·39	8·01
Alkaline earthy phosphate .	30·50	4·61	30·26	34·44	25·64

To tell the truth, fish guano has nothing in common but the name with the different guanos which have been described in this treatise, for it contains nitrogen in a different form and less assimilable than in guanos properly so called.

Whale Guano.—Guano is also prepared from whale debris; this product is similar to the preceding. Whale flesh contains in the fresh state about 5 per cent of nitrogen, and in the dry fat-extracted state about 14 per cent. The bones of the whale contain 3½ per cent of nitrogen and 23 per cent of phosphoric acid.

Crab Guano approaches fish guano. It is prepared from a species of sea-crab or lobster, of which there is enormous consumption on the coast of the North Sea. They are steamed, the substance pressed, then it is roasted on plates, and finally reduced to fine powder by grinding like fish guano. It is in the form of a bright yellow powder mixed with fragments of shells, and contains on an average 8 per cent of nitrogen and 3 per cent of phosphoric acid. There is also a manufactory of crab guano at Oporto, Portugal.

To appreciate the fertilizing value of the manures just described, it must be borne in mind that the greater part of their nitrogen exists not under the form of readily decomposable gelatine, but as a horny substance, which moreover always retains a certain amount of fat. These manures therefore act slowly, after the style of raw bone dust; if spread in autumn they decompose sufficiently in the winter to become active in the spring, supposing always that they have not been buried too deeply. Meat meal and fish meal dissolved by sulphuric acid with equal nitrogen and phosphoric acid content are of the same value and produce the same effect as bone superphosphate; it is therefore more rational to use these manures in their soluble condition. The consumption of fish guano assumes every year a new extension. The best sorts are used to feed cattle and chickens, while the ordinary sorts are used as manure. The price in the market per 100 kilos. (say 2 cwt.) was the following at the end of December, 1907:—

Norwegian fish guano, 8 × 12 per cent = 22·80 to 23·10 francs.
British „ „ 8 × 9 „ = 21·55 to 20·85 „
„ „ „ 7 × 11 „ = 17·80 to 18 „

It would be necessary still to describe a large number of nitrogenous wastes, for substances of animal or vegetable origin when they are damaged and otherwise unutilizable may always be used for the manufacture of manure; but as these substances rarely occur on the market in sufficient quantity, it will suffice to indicate them with a richness in phosphoric acid and potash.

TABLE XCII.—SHOWING THE COMPOSITION OF NITROGENOUS MANURES.[1]

The substances contain per 100 lb.	Nitrogen. lb.	Phosphoric acid. lb.	Potash. lb.	Nitrogen in dry substance. lb.
Nitrate of soda . .	15·3-16·0	—	—	—
Nitrate of potash . .	13·6-13·7	—	45·1-46·6	—
Nitrate of soda and of potash	14·8-15·2	—	undetermined	—
Sal ammonia . . .	19·6-20·9	—	—	—
Dried blood . . .	14·0-15·0	—	—	—
Meat meal . . .	14·5 about	—	—	—
Hoof and horn dust . .	13-16	—	—	—
Wool rags . . .	variable	—	—	—
Leather shavings disintegrated . . .	5-9·30	—	—	—
Bullocks' hair . . .	13·78	—	—	—
Cheese	4·53	—	—	—
Colombine . . .	8·39	1·15	0·25	8·42
Silkworm litter 5th and 6th period . . .	3·28	—	0·15	6·64
Beetles	3·29	0·4-0·7	?	10·000
White worms . . .	7·92	?	?	7·92
Greaves in cakes in marketable condition . .	11·87	—	—	12·5-15
Fish waste . . .	5-7	2-3	—	7·6
Nitrate of soda pure .	16·47	—	—	—
,, potash pure .	13·86	—	46·53	—
Sulphate of ammonia pure	21·21	—	—	—
Ammonium chloride pure .	26·17	—	—	—

[1] The nitrogen in several of these nitrogenous manures is more than usually high, almost double that of ordinary commercial samples, e.g. meat meal, greaves, etc. No table like this is a guide to the composition of any given sample on the market, the real value of which actual analysis can alone decide. —Tr.

CHAPTER XVI.

POTASSIC MANURES.

Preliminary Remarks.—The ash of plants consists for the most part of carbonate of potash, the caustic and detergent properties of which were bound to attract attention from the very beginning of civilization. And as a matter of fact the ancients knew this substance and employed it in domestic economy as well as in industry. Aristotle described the manner of extracting potash from the ash of plants. His process is still in use in certain countries. It consists in submitting the ash to a series of washings with water, concentrating the lye by evaporation, and in calcining the residual salt. As plants only leave a small amount of ash, and as this does not wholly consist of carbonate of potash, it is clear that the yield of potash cannot be very great. The plants the most rich in potash are the following :—

TABLE XCIII.—POTASH CONTENT OF VARIOUS PLANTS.

	Potash in 1000 parts.		Potash in 1000 parts.
Pine	0·45	Fern	6·26
Poplar	0·75	Reeds	7·22
Beech	1·45	Maize stalks	17·50
Oak	1·53	Sunflower stalks	20·00
Willow	2·85	Chrysanthemum	25·00
Alder	3·90	Nettle	25·03
Wheat straw	3·90	Vetches (tares) stalks	27·50
Thistles	5·00	Absinth stems	73·00
Vine	5·50	Fumitory	79·00
Barley straw	5·80		

In this category some plants will be remarked as very rich in potash, such as fumitory, absinth. Did not some persons have the idea about 1850 of cultivating them to extract the potash? Thus, in Sardinia, a plant was cultivated called in common language *glacialo* (Mesembryanthemum cristallineum) so as to obtain potash by burning it. The analysis of the ash of this plant, cultivated in *le Nord*, gave 30

per cent of carbonate of potash and 6 per cent of carbonate of soda, and sodium chloride. To appreciate the economic bearing of this idea, it will suffice to recall that plants can only draw potash from the soil, and that by growing potash-loving plants too often on the same ground it would soon become exhausted and sterile, unless the amount of potash extracted by the plants were restored. But then that would be going round in a bad circle: furnishing potash to the soil, as say potassium chloride, only to convert it into carbonate of potash in the plant which must be extracted by burning. It is unnecessary to dwell further on the subject.

Until comparatively recently plants were the sole source of potash, and as the industrial consumption of this plant was formerly much greater than to-day (they did not then know that soda could replace potash in most of its applications), the product was always insufficient to meet the wants of industry.

About the end of the eighteenth century the invention of Leblanc, which consisted in extracting soda from common salt, chloride of sodium came to deliver the farmer from the incalculable tribute which he was obliged to pay annually to industry under the form of potash. Some industries, however, especially glass manufacture, continue to use potash owing to the impossibility of their replacing it by soda. Attempts were then made to reduce the potash which occurs in abundance in a great number of insoluble and difficultly soluble minerals such as granite, porphyry, potash-felspar with 16·6 per cent of potash. But soon the discovery and the exploitation of the enormous deposits of potash salts of Stassfurt rendered this useless. Now, and for some time back, potash, or better carbonate of potash (for the word potash is no longer used except to denote the impure product), has been made in considerable quantities by the Leblanc process. The raw material used, the kainit, hard salt (p. 299), is supplied by the Stassfurt mines.

Stassfurt Salts.—In the Stassfurt mines very soluble potash salts occur in sufficient quantity to meet the wants of industry for an unlimited period. Far from having recourse, henceforth, to the farmer to borrow potash, industry is enabled to restore to him the enormous quantities which it had taken from him in the course of centuries. Encouraged by the geognostic conditions of the Stassfurt region, the first boring was begun on 3 April, 1839, in the hope of finding new deposits of common salt, the production of which was insufficient in the district. In the month of June, 1843, the first portions of salt were brought to the surface, and in 1851 a bed of salt 325 metres thick had been passed without reaching the bottom. The borehole was then 581 metres deep. The salt extracted from the borehole in 1843 had a density of 1·205, and the deeper the bed was penetrated the more the density increased. The analysis of the product gave the following results:—

TABLE XCIV.—ANALYSIS OF FIRST BOREHOLE SAMPLE OF STASSFURT POTASH SALTS.

	Per cent.
Magnesium sulphate	4·01
,, chloride	19·43
Potassium ,,	2·24
Common salt	5·62
	31·89

The poor content of this product in common salt caused a deep dejection which seemed likely to put an end to the researches. But as far back as 1848 Prof. Marchand of Leipsic asserted that the bed of salt ought to be pure and that the magnesium salts must come from the upper beds of the deposits. They commenced to dig the first pit (Von der Heydt) on 4 December, 1851, and the second (Von Manteuffel) on 31 January 1852. In 1856 they reached the exploitable bed at 333 metres (1092 feet) depth.

In 1858 the government of the Duchy of Anhalt likewise caused two pits to be excavated for the working of salt. A very pure bed of rock salt was found 300 metres (984 feet) in thickness. But after a few years it was seen that the bed of rock salt was far from representing the chief value of the mine. It was observed in fact that the saline beds which covered the common salt and from which the magnesium salts came which had been found in the depths of the bed formed enormous deposits, and contained an important proportion of potassium chloride. This product, which they did not know what to do with in the beginning, was destined to become a source of richness to agriculture. In 1854 a deposit of potash salts consisting of pure potassic chloride mixed with a little common salt was also discovered at Kaluse in Galicia. In 1869 a factory was built for its exploitation, but after a few years the crude salts brought to the surface only contained 1 per cent of potassium chloride. At the present time they there exploit a deposit of kainit (see under this heading) which is much more extensive than that of Stassfurt. In 1870 boring operations were conducted by Baron Douglas at about 3 km. (say 2 miles) from Stassfurt, which ended in discovering new deposits of potash salts, the working of which was soon begun. *Carnallite*, extracted from the mine and treated in the factory constructed on the working pit, is distinguished by its great purity. The enterprise was soon taken up by a limited liability company (Alkaliwerke Westerregeln), which continues to work it on a vast scale. Another exploitation of potash salts is that of New Stassfurt. It is interesting on account of the kainit which it supplies to the farmer. At Stassfurt itself the pit Ludwig II, which had been abandoned for a long time, has been reopened for the extraction of carnallite. There are still found a little further

away from Stassfurt the factories of Aschersleben at Bienenburg, of Thiederhall in Brunswick, the Solvay factories at Bernburg, and the Wilhelmshall pit near Auderbeck in the neighbourhood of Halberstadt. It would be futile to study here in detail the potash salt deposits of Stassfurt and elsewhere. The reader desirous of more ample information need only consult the special treatises on the subject. But as a knowledge of the manufacturing methods about to be described presupposes a knowledge of the minerals which enter into the composition of crude potash salts, it is deemed useful to describe them briefly.

Crude Potash Salts.—1. *Carnallite* forms the chief ingredient of crude potash salts. In the pure state it is clear as crystal, often iridescent ; generally however it is coloured red or reddish-brown by scales of crystallized oxide of iron. Its fracture is conchoidal, density 1·65. It is rarely found in distinct crystals in nature. Carnallite crystallizes in the rhombic system. The angles of the bases are 120° and 60°. The crystals of secondary formation met with in mines rarely have a tablet form. They are more often octahedral. Sometimes great masses of carnallite crystals are found so compressed by pressure that their surfaces appear concave ; the crystalline form is, however, quite distinct. Pure carnallite responds to the formula $KCl + MgCl_2 + 6H_2O$, and contains :—

TABLE XCV.—ANALYSIS OF CARNALLITE.

	Per cent.
Potassium chloride	26·76
Magnesium „	34·50
Water	38·74
	100·00

100 parts of water at 18·75° C. (66·75° F.) dissolve 64·5 parts.

2. *Sylvine* or *Sylvinite* is a natural product resulting from the decomposition of carnallite, and consists mostly of pure potassium chloride. Freed from the common salt with which it is mixed, it has the composition represented by the formula KCl, and contains in the pure state :—

TABLE XCVI.—ANALYSIS OF SYLVINITE (PURE).

	Per cent.
Chlorine	47·58
Potassium	52·42
	100·00

It is often colourless, rarely reddish or brown, brilliant like glass, with slightly conchoidal reflection, altogether resembling rock salt, crystallizing like the latter in regular cubes with an octahedral surface. Its fracture is angular, its density is 2·025. The potash salt found at Kalusz consists chiefly of sylvine ; it is coloured blue,

which generally only occurs with rock salt; according to certain authors, however, this coloration is due to admixture with blue rock salt. Sylvine as it comes from the mine has the following composition, according to Mercker :—

TABLE XCVII.—ANALYSIS OF SYLVINE AS IT COMES FROM THE MINE.

	Per cent.
Potassium chloride	30·55
Sodium ,,	46·05
Magnesium ,,	2·54
Potassium sulphate	6·97
Magnesium ,,	4·80
Gypsum	1·80
Water and insoluble	7·29
	100·00

Its potash content is 23·04.

3. *Kainit* is met with in large quantities, chiefly in the Leopoldshall mine and at New Stassfurt. A deposit of more than 25 metres (82 feet) has been found at Kalusz of almost pure kainit. It is colourless, or yellow to reddish or even a very dark brown. It is very hard in comparison with the other minerals mentioned in this chapter. Its density is 2·131. Its fracture has a crystalline lustre; it rarely gives true crystals. It contains, according to Reichardt :—

TABLE XCVIII.—SHOWING ANALYSIS OF KAINIT. (REICHARDT.)

Potash	17·37		
Soda	5·90		
Magnesia	14·76		
Sulphuric acid (SO_3)	30·00		
Chlorine	18·56		
Insoluble	0·22		
	86·81		
Less oxygen of the chlorine	4·18		
	82·63		
Water	17·37		
	100·00		
		or	
		Sulphate of potash 32·12	54·99
		,, magnesia 22·87	
		Magnesium chloride	16·95
		Water	17·37
		As impurities: Common salt	9·90
		Insoluble	0·22

Pure kainit responds to the formula—

$$K_2SO_4 + MgSO_4 + MgCl_2 + H_2O.$$

Kainit is, therefore, a double sulphate of potassium and magnesium combined with magnesium chloride. It forms, therefore, a peculiar compound, which no one as yet has succeeded in reproducing artificially like sylvine and carnallite. Its mode of formation is thus uncertain; it is supposed, however, that it results from the action of water on a mixture of carnallite and kieserite found in the salt

deposit. Kainit, as it is extracted in considerable quantities from the Leopoldshall, New Stassfurt and Kalusz mines, is freed as much as possible from common salt intercalated with it, then it is reduced to fine granules in a salt mill. It is put on the market as ground kainit, and contains on an average 65 to 75 per cent of pure kainit or 23 per cent of sulphate of potash (equal to 12·4 per cent of potassium).[1] The impurities consist chiefly of common salt and clay. Formerly, kainit was calcined and ground. This process has been abandoned in the Stassfurt factories. As it readily cakes and is then very difficult to break up, it has been mixed, on the advice of Fleischer, with 2·5 per cent of peat powder, which prevents this drawback. The same means is used for other potash salts when they are sold for manure.[2]

4. *Schoenite* is the double sulphate of potassium and magnesium and responds to the formula $K_2SO_4 + MgSO_4 + 6H_2O$. Its formation at the expense of the kainit by elimination of the chloride of magnesium would therefore be very plausible; its existence as a mineral is not established with certainty. Artificial schoenite will be described further on.

5. *Polyhalite.*—It is found in veins of 26 to 33 metres thick in the deposits of rock salt. It is mostly amorphous, rarely crystalline, of a grey colour and conchoidal fracture. Density 2·72.

TABLE XCIX.—ANALYSIS OF POLYHALITE.

	Per cent.
Potassium sulphate	27·90
Magnesium ,,	19·76
Calcium ,,	42·64
Water	5·75
Common salt and impurities	3·49
	99·54

[1] Should be, potassium equal to 12·4 per cent of potassium oxide K_2O.—Tr.

[2] The breaking up of kainit is a costly job. It should not be stored in bags piled one on the top of the other, but on arrival it should be shot in a dry place, covered in of course, and with a smooth dry floor. It can be brought from there readily in a barrow to where it is wanted by one man, whereas it takes two men to lug and tug about the caked bags and cut them open with a knife to get out the kainit solid as a rock, and then the tiresome job begins of pounding it with wooden mallets to break it up, and the small amount a couple of men can break up and screen in a day is well known to those who have been kept waiting for it to complete the ingredients in a heap that is to be dry mixed. A little better progress is made with the disintegrator, but even then it is a heart-rending job, as no sooner is the disintegrator started and well under weigh after a stoppage than the naturally moist kainit again blocks it. The advice of the translator is therefore to shoot the bags at the outset. The pressure cannot find vent without bursting the bags, therefore the kainit must consolidate and perforce cake into a solid as hard as in the original rock. The store should be an oblong building with the door in one end, and the concrete floor should rise gradually to the far end, where kainit and other water-soluble products should be stored beyond the reach of floods.—Tr.

It responds therefore to the formula—

$$K_2SO_4 + MgSO_4 + 2CaSO_4 + 2H_2O.$$

When treated with water it is the potassium salt which preferably dissolves, whilst the magnesium sulphate and the calcium sulphate remain in great part undissolved. Before being discovered in the Stassfurt mines polyhalite had been already met with in different places at Ischl, Hallein, Berchtesgaben, etc., partly as rhombic crystals or fibres or minute crystalline rods.

6. *Krugite* has a chemical composition similar to polyhalite. It responds to the formula—

$$K_2SO_4 + MgSO_4 + 4CaSO_4 + 2H_2O.$$

TABLE C.—ANALYSIS OF KRUGITE. (MERCKER.)

	Per cent.
Potassium sulphate	18·60
Magnesium „	14·70
Calcium „	61·00
Water	4·20
Common salt	1·50
	100·00

Density 2·801.

It now remains to describe the processes used to extract from these minerals the whole series of products supplied to agriculture as potassic manures.

Manufacture of Potassium Chloride [muriate of potash].—The crude salt treated consists of a mixture of all the salts described above. However, carnallite predominates; it forms 50 to 60 per cent of the crude salt, equal to a potassium chloride content of 13 to 17 per cent. The processes now used in the treatment of the crude salt in the manufacture of more pure potash salts (potassium chloride) are based essentially on the property of carnallite to decompose in presence of water into potassium chloride and magnesium chloride; it is therefore dissolved and potassium chloride separated from the solution by crystallization. The process is in itself very simple; what complicates it is the presence of quite a series of foreign salts accompanying the carnallite, the most important of which are rock salt [NaCl], in the proportion of 20 to 25 per cent, and kieserite [$MgSO_4 + H_2O$], which forms 15 to 20 per cent of the crude salt. Other minerals, such as kainit, polyhalite, tachydrite $CaCl_2 + 2MgCl_2 + 12H_2O$, etc., are rarely met with in large proportion, but they then are very troublesome in the process.

Crushing the Crude Salts.—As the mines deliver the crude salt in big lumps (in the beginning they delivered them ground), they must be crushed before being treated. Formerly they were satisfied with crushing lumps by blows from a mallet with a long handle,

but now all the factories have laid down mechanical crushers for the purpose; the machine most used is the jaw-breaker crusher already described.

Dissolving the Crude Salts.—The salt is then fed into a pan, in which it is dissolved. The crushed salt falls from the mill into the receiver of a cup-elevator, which delivers it directly into the dissolving pans or into a wrought-iron shoot. The elevator is driven by a shaft on which is mounted the belt pulley. The dissolving pan is of riveted wrought-iron of a cylindrical form ending in a conical bottom. At the beginning of the cone is a perforated short bottom intended to retain the residues from the salt. These residues are run out through a manhole. The solution is drawn off by a tap, the pan is steam heated. In the early days the Stassfurt and Leopoldshall factories wrought in an appreciably uniform style, but lately they have adopted different methods more conformable to the interests of each factory. The oldest method, still much employed, is the following: The dissolving pan is first partly charged with water, mother liquor, which is termed II, with residual solution I (see further on) and with clarified solution III (see further on). After having brought this mixture to the boil, by direct injection of steam, the crude salt is fed into the elevator, whilst continuing to boil without interruption; the carnallite soon dissolves and therefore the density of the solution increases gradually; the escaping steam by a suitable arrangement sets the liquid in motion and mixes its different components. When the density of the liquid, taken on a boiling sample, reaches 32° to 33° B., the elevator is stopped, the steam turned off and the solution run out; the residue remaining in the pan contains a large proportion of kieserite, common salt, and about 2 to 4 per cent of potash salts. In a great number of factories this residue is again taken up and boiled with a little water; the solution thus obtained (I) consists therefore chiefly of common salt, a little magnesium chloride and magnesium sulphate. Its potassium content varies from 3 to 7 calculated as potassium chloride; it is used solely to dissolve fresh quantities of crude salt. The proportions of the different solutions as well as the densities vary with the factory. The residues are thus more or less abundant and retain more or less salts. The best results are obtained by preparing solutions of 32° B. with lower densities; they retain a large amount of common salt; when on the contrary their density is higher, they retain less common salt and more potassium chloride.

Clarification.—Crude solution as it comes from the pan is soiled with impurities; it is therefore run into clarification basins, where it remains for about forty-five minutes. These basins are rectangular, of riveted wrought-iron, fitted with two apertures, from one of which the clarified solution is run off, and from the other the sludge. To prevent the clarified solution carrying the

sludge with it, different arrangements have been made to retain it. After the clarified solution has been run off, it is led through a wrought-iron gutter into underground crystallizers. As the solution cools in flowing through the gutters, it deposits a certain amount of salt containing 45 to 50 per cent of potassium chloride. This gutter salt is most generally used in manure manufacture. It is generally treated with potassium chloride of a higher strength.

Crystallization.—The crystallizers in which the solution cools and forms crystals of potassium chloride are of riveted wrought-iron like the clarification basins; they vary in size and shape, sometimes flat because the solution cools more quickly therein, sometimes deep because they occupy less space and yield larger crystals. When the solution is cold, which takes two to four days, the mother liquor II is decanted from the crystals of potassium chloride; it is run off by the gutters fixed under the crystallizers into wrought-iron basins or into masonry ones lined with cement. It is used either to dissolve the crude salt or treated directly as will be described further on. The potassium salt which is deposited in the crystallizers consists of a mixture of potassium chloride and common salt; it is still soiled by adhering mother liquor. It crystallizes in the same form as sylvine, with this difference that the crystals are not always perfect; their size depends chiefly on the density of the solution of crude salt. When that has a density of 32° to 33° B., or a still weaker density, crystals often one centimetre wide, of a pearly lustre, are obtained. When the solution is more dense, say about 33° to 35° B., it forms soft crystalline needles. It is clear that the size of these crystals must considerably affect the purity of the potassium chloride, as attenuated crystals must retain more mother liquor than large ones, and that consequently they contain more magnesium chloride. The impure, fine, granular salt often only contains but 60 per cent of potassium chloride, whilst the salt with large crystals yields on analysis:—

TABLE CI.—ANALYSIS OF CRYSTALS FROM POTASH SALT CRYSTALLIZERS.

	Per cent.
Insoluble	0·0876
Magnesium sulphate	1·2468
,, chloride	6·9072
Potassium ,,	68·1504
Common salt	23·5560
	99·9480

It may be remarked in passing that the salt that is deposited on the sides of the crystallizers is always more pure than that deposited at the bottom. To obtain high strength products, a portion of the two sorts may be taken, especially for continuing the treatment.

Clarifying.—As potassium chloride of 60 to 70 per cent strength is hardly marketable, it is necessary to submit it to new treatment —*clarification*. For this purpose it is run into vats termed clarifying vats, fitted with a double bottom covered by cloth or with a network of osiers. It is covered with water, so that the water is 2 to 3 centimetres above that of the salt, and left in contact 5 to 6 hours; then the clarified solution III is run off through a bung-hole in the bottom of the vat. This liquid runs into a special basin, from which it is run into the dissolving pans by a pump. The liquid from the above clarification of 30° B. contains :—

TABLE CII.—ANALYSIS OF MOTHER LIQUOR FROM CLARIFICATION OF POTASH SALTS.

Water	72·212
Magnesium sulphate	1·659
,, chloride	11·730
Potassium ,, ...	5·930
Common salt	8·469
	100·000

If the potassium chloride be not sufficiently enriched by a single clarification, this operation is repeated once or twice until the salt contains at least 80 per cent of dry potassium chloride. The above clarifying liquor constitutes a saturated solution. Now a solution of this nature contains at 15° C. 25 per cent KCl when it is prepared from pure potassium chloride, 27 per cent NaCl when it is made from common salt. If these figures be compared with those of the above analysis, it will be seen that the magnesium chloride interferes with the solution of both the potassium chloride and with the common salt. Now as the object of clarification is precisely to eliminate this latter, it follows that a potassium salt with low magnesium chloride content, consequently large-grained, will be more easy to purify in this way than a salt with high magnesium chloride content, fine-grained crystals. But clarification is a costly operation because its object is to redissolve a portion of the finished salt, therefore to work economically it must be done in such a way as to clarify as little as possible, that is to say to produce large-grained crystals as far as possible. Starting from the salt analysed above, an 80 per cent product would be obtained by a single clarification, whilst a fine-grained salt often requires two, sometimes three, clarifications to get a product of the same strength. It is clear that by this operation 95 per cent products and higher may be obtained.

Treatment of the Mother Liquor from the Potassium Chloride.—The mother liquor not used for dissolving is concentrated by evaporation, for it still contains an important amount of potassium chloride. It has a density of about 32° B., and contains :—

TABLE CIII.—ANALYSIS OF MOTHER LIQUOR FROM POTASSIUM CHLORIDE.

Magnesium sulphate	2·3 to 2·6
,, chloride	19·5 to 20·9
Potassium ,,	5·1 to 6
Common salt	2 to 3

In the evaporation the greater part of the common salt separates out because it is less soluble when hot than when cold, at the same time as the double salt of potassium and magnesium (schoenite), which is hardly soluble. This mixture of residual salts often contains 7·5 per cent of potassium, which corresponds to 12 per cent of potassium chloride, or to 14 per cent of potassium sulphate. It is utilized by either extracting the common salt from it or by converting it into manure of low strength. In rational manufacture the residual salt should be washed in the pan itself; for this purpose the mother liquor II is used, as the salt as well as the pan itself is still very hot. When the evaporated solution is run off, the mother liquor with which the pan is drenched heats rapidly and then dissolves the greater part of the potassium salt which is still contained therein. This solution is facilitated by stirring. When the density of the solution determined whilst boiling reaches 34·5 to 35° B., it is run through wrought-iron gutters into special crystallizers, where it deposits not potassium chloride, but a salt with tetrahedral crystals, the composition of which is analogous to carnallite. If the solution was sufficiently concentrated, the liquid which flows from the carnallite crystals (final liquid) only contains 1 to 1·5 per cent of potassium chloride, and in addition :—

	Per cent.
Magnesium chloride	26 to 28
,, sulphate	4
Common salt	2 „ 4

In certain factories the bromine is extracted, in others the magnesia. The artificial carnallite thus obtained is dissolved in water in smaller pans than those used to dissolve the crude salt. The solution testing 32 to 33° B. is run into vats, where it deposits potassium chloride more pure than that got from the crude salt. The mother liquor of this salt is added to the first. As the carnallite from whence it comes contains less common salt than the crude salt, this mother liquor yields little residual salt. The salt yielded by artificial carnallite is clarified with very little water, and then yields very high strength potassium chloride (95 to 98 per cent).

Drying the Chloride of Potassium.—In most factories potassium chloride is dried in reverberatory furnaces. In recently erected factories the drying is conducted in cylindrical coil-heated tanks, in which an agitator with blades revolves, and a roller compressor.

When the shaft revolves the blades turn up the salt, and the roller which follows makes them into a cake again, so that the surfaces are continually renewed. When the drying is finished the salt is run out through a shoot and bagged up. In a general way factories which work according to the processes described above are content with producing 80 per cent potassium chloride; they rarely push the clarifications so far as to make 97 to 98 per cent products, although the potassium chlorides dissolved by the clarification can be recovered immediately in the crystallizers, whilst the mother liquor is used to dissolve the crude salt. To obtain 98 per cent salt without effort, the method of dissolving the raw salt is altered. The mother liquor, the small amount of clarifying liquor and finally the liquor used to boil the residual salt, are alone used as solvent; all addition of water is avoided. After having brought the solvent solution in the pan to the boil, the raw salt is run in as before and the whole boiled without interruption until the solution tests 35 to 36° B. At that density the carnallite in the crude salt easily dissolves if the liquid be hot enough, i.e. if the steam be of sufficient tension. Certain factories insert an agitator whose action contributes to mix the solution, consequently to obtain a better result from the crude salt. Nevertheless, the residue is sometimes still rich in potassium chloride; it is boiled a second time with pure mother liquor. The solution so obtained is clarified in the same way as in the first method; on cooling it deposits not potassium chloride but carnallite, which is allowed to drain and then dissolved in boiling water to extract the potassium chloride. As common salt as well as kieserite only dissolves slightly when hot in a concentrated solution of magnesium chloride, whilst potassium chloride is very soluble therein, it is clear that the solution prepared by this process should contain very little common salt, and also that the carnallite which crystallizes therein should contain very little, and the chloride of potassium furnished by the latter should be of high strength. This method, however, has the drawback of yielding a large amount of carnallite, the removal and solution of which require much labour and steam and consequently fuel. This drawback is obviated by diluting the solution which flows from the clarification vats with water, so that after complete cooling it yields chloride of potassium of high strength directly, and no longer carnallite. In this way the crystallization and solution of carnallite are conducted in a single operation. The advantages of this method of working are evident. Instead of treating as before two different solutions and two different salts, only a single solution and a single salt have now to be treated. The potassium chloride so produced is so pure that when it is freed from magnesium chloride by a little water it only contains 0·5 per cent of common salt, all the rest is potassium chloride with a little moisture and some slight impurities.

Potassium Sulphate.—This salt is manufactured at Stassfurt, by drenching potassium chloride with sulphuric acid and calcining in a reverberatory furnace. The reaction which takes place is the same as that used to manufacture sodium sulphate from common salt and sulphuric acid. First of all the material heats, gaseous hydrochloric acid is given off, and acid potassium sulphate formed according to the equation—

$$KCl + H_2SO_4 = HKSO_4 + HCl.$$

Afterwards, the temperature continuing to rise, the acid sulphate of potassium being weak acts on the remainder of the potassium chloride. A new disengagement of hydrochloric acid gas is produced, and finally potassium sulphate as a solid mass. This reaction is expressed by the equation—

$$KCl + HKSO_4 = K_2SO_4 + HCl.$$

As the potassium sulphate as it comes from the furnace is in big lumps, it must be crushed before delivery to farmers. In the same way as the price of potassium chloride is calculated on the basis of an 80 per cent salt, that of potassium sulphate is based on a 90 per cent salt, consequently 100 lb. of this product at 95 per cent equal 110 lb. at 90 per cent. Potassium sulphate of 96 per cent strength is worth about 2½d. more a cwt. on the 90 per cent basis than the product which only tests 90 per cent.

Double Sulphate of Potassium and Magnesium.—This product has already been mentioned as *schoenite*, but is never found in that form; it is manufactured in large quantities from kainit. It consists of equivalent quantities of potassium sulphate and of magnesium sulphate, and contains in the crystalline state six equivalents of water. The method of manufacture varies with the factories, but all processes are based on the lixiviation of the magnesium chloride and common salt from the kainit by hot saline solutions. The dried ground salt contains about 48 per cent of potassium sulphate corresponding to about 26 per cent of potassium, and it is put on the market with the guarantee of a maximum content of 2·5 per cent of chlorine. This salt is much used as a manure.

It possesses the following composition, according to Mercker :—

TABLE CIV.—ANALYSIS OF SCHOENITE. (MERCKER.)

	Per cent.
Potassium sulphate	50·4
Magnesium „	34·0
Common salt	2·5
Water	11·6

Its potassium content is therefore 27·2.

Double Carbonate of Potassium and Magnesium.—The salt contains 17 to 18 per cent of potassium; it consists chiefly, as its name indicates, of the carbonates of potassium and magnesium with

2 to 3 per cent of impurities, potassium chloride and potassium sulphate. This salt, therefore, contains very little chlorine and might perhaps be used as a fertilizer for tobacco. But the price of potassium is about double in it to what it is in potassium sulphate.

Potash not only acts as a manure but it retains the moisture in the soil. Certain potash salts absorb moisture and cake; kainit especially forms very hard blocks like stone. Spread in a thin layer it absorbs 2 per cent of moisture in twenty-four hours.

Calcined potash salts absorb from dry air up to 6 per cent of water, in five days 14 per cent, and up to 24 per cent in six days. To prevent them caking into a solid mass it suffices to add 2·5 per cent of peat powder; the mixture so prepared keeps for two months without drawback.

Other Fertilizing Salts.—The Stassfurt factories sometimes make a fertilizer from other waste not hitherto utilized. For this purpose the sludge deposited at the bottom of the clarification pans, which always contain a little potash, is used. 100 parts of calcined ground sludge contain :—

TABLE CV.—ANALYSIS OF SLUDGE FROM CLARIFICATION OF POTASH SALTS.

Insoluble (oxide of iron, sand, gypsum) .	6·34	
Calcium sulphate	8·67	
Double sulphate of potassium and magnesium ($MgSO_4 + K_2SO_4$) .	16·46	Equal to potassium.
Potassium chloride	11·01	5·27
Magnesium ,, ...	10·24	6·95
Common salt	45·51	
Water and loss	1·77	
Say 19·35 KCl or 22·54 sulphate of potash		
	100·00	12·22

Another product of this kind is furnished by the residual salt which contains about 12 per cent of potassium sulphate; as we have seen, this consists of sludge and especially of common salt.

A third salt likewise used as a fertilizer is that extracted from the gutters, which when dry contains about 50 per cent of potassium chloride, and 45 to 50 per cent of common salt.

All these salts are treated in the same way. They are dried in a reverberatory furnace by heating them to nearly the point of fusion, then they are crushed. Brown fertilizing salts with low potassium content are hardly met with now on the market. The salt from the gutters dried and ground is sold under the name of "manure salt, calcined and ground," with a minimum guarantee of 27 per cent of potassium. Lately a whole series of other potassic manures has been manufactured, but their high price is an obstacle to their sale. The composition of the different Stassfurt salts are summarized in the following table :—

TABLE CVI.—COMPOSITION OF STASSFURT POTASH SALTS.[1]

Name of the Salts present in 100 parts.	Sulphate of Potash K_2SO_4.	Potassium Chloride KCl.	Magnesium Sulphate M_gSO_4.	Magnesium Chloride M_gCl_2.	Sodium Chloride NaCl.	Calcium Sulphate $CaSO_4$.	Insoluble in Water.	Water.	Potash (pure) Content.	
									Average.	Guaranteed.
A. Crude Salts. (Natural products from the mines.)										
...init	21·3	2·0	14·5	12·4	31·6	1·7	0·8	12·7	12·8	12·4
...rnallite	—	15·5	12·1	21·5	22·4	1·9	0·5	26·1	9·8	9·0
...lvinite	1·5	26·3	2·4	2·6	56·7	2·8	3·2	4·5	17·4	12·4
...rgkieserite	—	11·8	21·5	17·2	26·7	0·8	1·3	20·7	7·5	—
(On demand the crude salts are delivered mixed with peat powder)										
B. Concentrated Salts. (Manufactured products.)										
...tassium sulphate 96 per cent	97·2	0·3	0·7	0·4	0·2	0·3	0·2	0·7	52·7	51·8
...tassium sulphate 90 „	90·6	1·6	2·7	1·0	1·2	0·4	0·3	2·2	49·9	48·6
...uble phosphate of potash and magnesia	50·4	—	34·0	—	2·5	0·9	0·6	11·6	27·2	25·9
...tassium chloride 90-95 per cent	—	91·7	0·2	0·2	7·1	—	0·2	0·6	57·9	56·8
...tassium chloride 80-85 „	—	83·5	0·4	0·3	14·5	—	0·2	1·1	52·7	50·5
...tassium chloride 70-75 „	1·7	72·5	0·8	0·6	21·2	0·2	0·5	2·5	46·6	44·1
...tassium salt for manure, minimum 20 per cent potash	2·0	31·6	10·6	5·3	40·2	2·1	4·0	4·2	21·0	20·0
...tassium salt for manure, minimum 30 per cent potash	1·2	47·6	9·4	4·8	26·2	2·2	3·5	5·1	30·6	30·0
...tassium salt for manure, minimum 40 per cent potash	1·9	62·5	4·2	2·1	20·2	2·4	3·1	3·6	40·4	40·0
...dicate of potash (martelline)	—	—	—	—	—	—	—	—	22·3	—

[1] Average of numerous analyses by the Potash Syndicate.

Commercial Brands of Potassium Chloride (*Muriate of Potash*). —The principal commercial brands of potassium chloride supplied by the Stassfurt factories are the following :—

(*a*) 70 to 75 per cent potassium chloride (muriate of potash) containing on an average 45 per cent of pure potash (K_2O) and 21 per cent of sodium chloride, 2·5 per cent of water, 1·7 per cent of sulphate of potash, 0·8 per cent of sulphate of magnesia.

(*b*) 80 to 85 per cent potassium chloride (muriate of potash) containing on an average 50 per cent of pure potash (K_2O), 14 per cent of sodium chloride and 1·1 of water, etc.

(*c*) 90 to 95 per cent potassium chloride (muriate of potash) containing 56·9 per cent of pure potash (K_2O), 7 per cent of sodium chloride and 0·6 per cent of water.

(*d*) 97 to 98 per cent of potassium chloride. It is the most concentrated product. For this latter certain factories guarantee 0·5 per cent of sodium chloride, for which an extra charge is made.

The selling price for all sorts is based on 100 kg. (220 lb.) at 80 per cent, bags included, that is to say that products with a plus value are brought to 80 per cent by calculation. An example will make this custom more plain. Suppose that the price of potassium chloride of 80 per cent be 9·40 francs, bags included, say 3s. 9d. the cwt. If the muriate bought is of a higher strength (say 95 per cent) it will cost 11·14 francs (say 4s. 6d. the cwt.), that is to say 100 kg. (220 lb.) of muriate at 95 per cent strength correspond to 118·75 kg. (261·25 lb.) of 80 per cent muriate. It is clear that the price increases proportionately with the purity of the muriate.

As to sulphate of potash the price is calculated on a 90 per cent basis. Consequently 100 kg. (220 lb.) of this product at 95 per cent equal 110 kg. (242 lb.) at 90 per cent. Sulphate of potash of a guaranteed strength of 96 per cent is worth about 0·50 francs (4·8d.) more per 110 kg. (220 lb.) or 2½d. more per cwt. (price based on this basis is price of 90 per cent) than the sulphate which only tests 90 per cent.

Remarks on the use of Potash Salts as Fertilizers.—As already seen, the Stassfurt mines furnish crude salts and refined salts as fertilizers. Which should be preferably used? This question is of great practical importance which farmers are far from doubting if we are to believe the emphatic puffs of kainit dealers and the other societies "for the encouragement" (so-called) of the diffusion of manures. In the last thirty years the consumption of potassic manures has progressed considerably, but instead of using pure salts the farmer has chiefly used the crude salts, kainit and carnallite. As will be seen in the analyses given below, crude potash salts contain besides potash, sodium chloride, magnesium chloride, etc.; in fact they contain much more chlorine than potash.

The following according to analyses now old are the chlorine content of crude Stassfurt salts :—

TABLE CVII.—CHLORINE CONTENT OF CRUDE POTASH SALTS.

	Percentage of		Parts of Chlorine per 100 parts of Potash.
	Potash K_2O.	Chlorine.	
Kieserite	7·44	34·67	46·60
Carnallite	9·78	37·03	37·86
Ordinary fertilizing salts	12·22	30·53	25·00
Kainit	12·76	31·21	24·45
Sylvinit	23·04	44·39	19·27
Fertilizing salt, good quality	31·55	52·33	16·59
Muriate of potash, 80 per cent	52·05	48·68	9·35
,, ,, 90 ,,	58·37	47·67	8·16
,, ,, 98 ,,	61·48	46·95	7·59
Double sulphate of potassium and magnesium	27·22	1·52	5·5
Potassium sulphate, 90 per cent	49·93	2·23	4·5
,, 96 ,,	52·68	0·56	1·0
Carbonate of magnesium and potassium	17·18	?	?

More recent analyses of kainit in the agricultural experiment stations have shown for a long time that the proportion of chlorine has been continually increasing.

Thus, in 1895, B. Sjollemay found 35·8 of chlorine. In 1896, Adolphe Mayer found still higher figures. In 1908, chlorine and potash were estimated in fifty-nine samples. A single sample alone gave the same chlorine content as formerly :—

	Per cent.
5 samples	30 to 35
18 ,,	35 to 40
24 ,,	40 to 45
9 ,,	45 to 50
2 ,,	over 50

It is, therefore, established that kainit has not the same composition as formerly. It would appear to be mixed with minerals rich in potash and with a high chlorine content. A more complete analysis of the kainit showed that some samples only contained 1·50 per cent of sulphuric acid. Potassium chloride (muriate of potash) contains 50 per cent of potash and 50 per cent of chlorine. In a number of samples of kainit the chlorine content was also 50 per cent, but the potash content was only one-fourth of the amount contained in potassium chloride. In this way it would be necessary to use four times more of a manure of this kind to obtain

the same result than with muriate of potash. But the high percentage of chlorine in crude potash salts has other drawbacks, so much the greater because it has been forgotten to point them out. Chlorine exerts a disastrous influence on the physical constitution of the soil and on vegetation. Moreover, it cannot be denied that the secondary salts which accompany the potash strongly attack the reserves of fertilizing ingredients in the soil. The potash is evidently absorbed by the soil, if it be supplied to it as chloride or as sulphate of potassium; the latter combines with the silica of the silicates of lime, soda, and magnesia, whilst the secondary elements such as the chlorine in muriate of potash, sulphuric acid in sulphate of potash, combine with lime, soda, and magnesia. In the first place calcium chloride is formed, in the second calcium sulphate. But as calcium chloride is very soluble in water, it is carried by it down into the depths of the soil, and thus lost to the crop. This fact agrees perfectly with that other fact which has been established, viz. that potassic manures, especially the chlorinated manures, rob the soil of its lime; thus 100 kg. (220 lb.) of kainit, containing 31 kg. (78·2 lb.) of chlorine, cause the soil to lose 100 kg. (220 lb.) of lime. It follows, therefore, that the use of potassic manures entails the use of calcareous manures. Mercker advises to apply to the soil as much quick-lime as potash salts. It thus follows that the comparative cheapness of crude potash salts, such as kainit and sylvinite, is nothing but a snare, because to take everything into account, the price of these salts ought to be increased by the price of the lime, the loss of which they entail. In marshy land the simultaneous application of lime is particularly necessary. In such soils in fact the potash salts are rapidly robbed of their acid in such a way that in the absence of lime the chlorine forms free hydrochloric acid which poisons the plant. Lime, moreover, is an indispensable corrective to the secondary effects which crude potash salts never fail to produce, the most important of which is the prevention of nitrification in the soil. Holdefleiss, in experiments with farmyard dung, completely suppressed it by means of potash salts. The solvent action exerted by the secondary salts of potassic manures is very well brought out in Lawes and Gilbert's experiments. They obtained an increased yield with salts free from potash. The plots experimented on received every year from 1854, 4 kg. of sulphate of ammonia and 350 kg. of superphosphate. The following amount of salts were added per hectare :—

TABLE CVIII.—EFFECT OF SOLUBLE MINERAL SALTS ON GRAIN CROPS.

	Weight of Crops in Kilogrammes per Hectare.					
	1852-70.		1870-89.		1890.	
	Grain.	Straw.	Grain.	Straw.	Grain.	Straw.
No salt	1868	3404	1417	2543	2036	3737
400 kg. sulphate of potash .	2295	4114	1789	3190	2500	4585
,, ,, soda . .	2275	4240	1883	4674	2775	5602
,, ,, magnesia .	2289	4051	1882	3291	2369	4333

It will be seen from these figures that salts free from potash have furnished yields almost more heavy than the pure potash salt. These salts, therefore, have mobilized the reserves of fertilizing ingredients in the soil, so as to bring them to the support of the plant. The soil has thus been, in a way, robbed of its normal reserve in favour of a few crops. This robbing of the soil would have been brought out in a more serious manner if the experimenters, instead of using sulphates, had used chlorides, because then it would be complicated by loss of lime. In fact, it is not stated that here again the nutritive substances of plants including phosphoric acid may not be rendered soluble and consequently carried down into the depths of the soil. The same phenomena must perforce occur with kainit, sylvinite and carnallite; the comparative low proportion of pure potash salts makes their action almost nil compared with that of the secondary salts which accompany it in these products. There is here a very interesting subject for study by agronomists. It would be specially useful to find if drainage water contains fertilizing substances in those cases where crude potash salts are used. Amongst these fertilizing substances, phosphoric acid may be found, for we must not forget that phosphate of lime is soluble in a great number of saline solutions. There might also be found in the drainage water as much potash as was spread on the soil, which would prove that the use of crude potash salts as manure would be absolutely illusory. It is probable that there will be no delay in giving up the use of crude potash salts, so as to keep solely to the pure potash salts, in spite of their higher price, when the devastating action of the secondary elements which accompany the potash in the crude salts is realized.[1]

[1] Whilst muriate of potash should be used sparingly and with the greatest discrimination, kainit when fairly free from chlorine is a safe and most valuable manure, especially for potatoes. The translator considers it sound practice to

Potash Salts Deposits of Alsace.—Deposits of potash have been discovered in Alsace. They consist chiefly of sylvinite. According to report from the President of the district of Upper Alsace, the deposits of rock salt and of potash occur in the *Tertiary*. The territory in question extends to about 200 sq. km. (say 125 square miles). It is bounded on the north by the line Regisheim-Soultz, to the west by the line Soultz Berrweiler-Schweighausen, to the south by the line Schweighausen-Neidermorschweiler-Ile Napoleon, and to the east by the line Ile Napoleon-Ensisheim-Regisheim. The total thickness of the deposit is estimated at 200 metres (656 feet), and the beds of potash salt are included therein, fairly regularly. These deposits appear destined to play a part in the German potash industry.

Manufacture of Potash from Felspar and other Potassic Minerals.—The felspar is finely crushed, beaten up with water, then run into a wooden vat placed in a large receiver of any material. The outside receiver is then filled; the inside receiver is then connected with the positive pole and the outside receiver with the negative pole of an electric current. This partially liberates the potash, the soda and the other soluble bases, freeing them from the compounds which they form with silica. The soluble bases traverse the wooden wall of the interior vessel and pass into the water of the exterior vessel which they render alkaline. However, the felspar soon ceases to decompose. To render the decomposition more rapid and more permanent the mass in the interior vessel is continually stirred or hydrofluoric acid added. To obtain nitrates, sulphates, chlorides, in place of caustic alkali, it suffices to add the corresponding acids into the water of the outside receiver. American patent No. 851,922 of 30 April, 1907.

Manufacture of Potash in the Caucasus.—The manufacture of potash is an accessory industry of the cultivation of sunflower, for the ashes of the stem and the branches of sunflower yield the raw material. The first potash factory was established in 1899 at Maikopp, by Schaponalow. Difficulties occurred at first because experience was awanting. But gradually the conditions of production improved, and fresh factories were started. According to the official statistics in 1906, eleven factories produced 475,563 poods of potash. According to information supplied by the manufacturers twenty-four factories were at work in 1907, and some of them produced several thousands and up to 200,000 poods of potash. The total production of these factories was from 700,000 to 900,000 poods, representing a value of 22,000,000 roubles. The stems of the

add 1 cwt. to 2 cwts. of such kainit per ton to all compound manures, that is when it can be done without lowering the guaranteed percentage of the phosphoric acid and nitrogen below the minimum guarantee. Potatoes respond in a very remarkable manner to such a manure.—Tr.

sunflower are generally burnt by the farmers themselves. But certain manufacturers also burn the plant and buy the stems of 10,000 to 15,000 deciatines, for which they pay 3 to 4 roubles per deciatine. A deciatine of sunflower yields in good ground 200 to 300 poods of stems and in bad ground 100 poods only, from which 3 to 5 per cent of ashes may be extracted, and 3 to 4 poods of ashes give one pound of potash. The percentage of carbonate of potash is 20 to 35 per cent. The appearance of the ash is improved by a few turns of the wrist, by throwing the salt in the fire for instance, which causes the ash to fuse and gives it a vitreous appearance.

When the sunflower harvest is finished the stems are burnt. The purchase of ashes is finished in September, whilst the manufacture of potash lasts five to six months. The price of the ashes up to now has been 35 copecks, but owing to competition it has risen to 40 and 60 copecks per pood. The manufacture of potash is conducted in a very primitive fashion: it consists in lixivating the ashes, methodically concentrating the lyes, and in calcining the product. The product is packed in casks of 30 to 40 poods. The analysis of a potash from Kuban gave (per cent) water, 1·74; carbonate of potash, 89; carbonate of soda, 5·0; sulphate of potash, 2·01; potassium chloride, 6·51; insoluble, etc., by difference, 0·74; the usual potassium carbonate content is 90 to 91. It is dealt with on a basis of 90 per cent with 2 per cent margin at least. Three-fourths of the potash is exported to Hamburg, London and New York.

CHAPTER XVII.

TRANSFERENCE AND HANDLING OF RAW MATERIALS AND FINISHED PRODUCTS.

The economic handling of raw materials, fuel, and finished products is one of the most important problems which the manufacturer—desirous of coping with competition, which becomes each day more bitter and better equipped—has to solve. But up to now it was exceedingly difficult to find a universal system of automatic transport adapting itself to the varying exigencies of different factories, and for a long time it was only possible to devise special installations for each case according to the nature of the materials to be conveyed. To difficulties of this nature another had to be added arising from the plan of the factories themselves. The greater part of them, as is well known, had a very modest beginning. They have developed gradually and have increased their production in a measure quite out of proportion with the working space at their disposal, so much so that there is no room for installing conveyors. These are reduced to the installing of lifts and small rails of the Decauville type. The systems used for conveying raw materials already warehoused or to be warehoused may be reduced to three: the continuous system, the funicular suspended rails, and the electric suspended rails, which hardly go back fifteen years. The continuous system is already known, having been in use for a long time in all industries. It will suffice to point out a very neat improvement which has lately been made by Ad. Bleichert and Co. In continuous systems, whether the conveyors are bands or cups, work is confined to the same plane. All cup or chain conveyors known up to now other than those on the Ad. Bleichert and Co's system have the drawback of working in the same plane, and consequently entail a transhipment of the materials when it is desired to convey the materials in different planes. This transhipment entails costly plant, consumes motive power uselessly, and exhausts the material. The mono-rail cup system of Ad. Bleichert and Co. suppresses these drawbacks, for the cup-chain continues to pass from one plane to another by aid of suitable guides. Fig. 54 shows the section of the cups of this ingenious system. Figs. 55 and 56 are photographs of installations of this system at work. Fig. 57 is an application of

this cup-chain to the handling of fuel and raw material in a chemical factory. This firm has likewise brought the electric automatic systems with intermittent charges to such perfection that they have spread enormously for some time back in Europe in metallurgical works and chemical factories. This process of automatic electric handling consists in causing an automatic car to which is suspended a bin to convey the material to run over an aerial railway. The current is led to this electric car by a bronze wire. Fig. 58 represents this system, which has this great advantage, that any desired shape may be given in a horizontal plane to the rigid aerial railway, so that it can go round the multiple obstructions which it meets not only in old factories but even in those still under construction. An electric automotor truck such as is shown in Fig. 58 can turn in curves of two metres radius. The Americans, it is true, were the promoters of a system called "Telpherage," which was likewise based on the conveyance of heavy unitary loads on

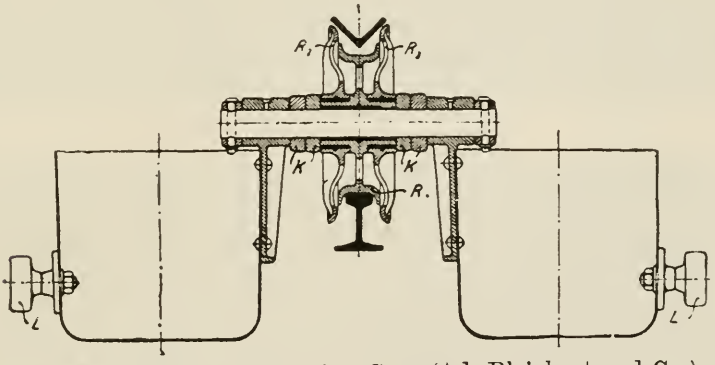
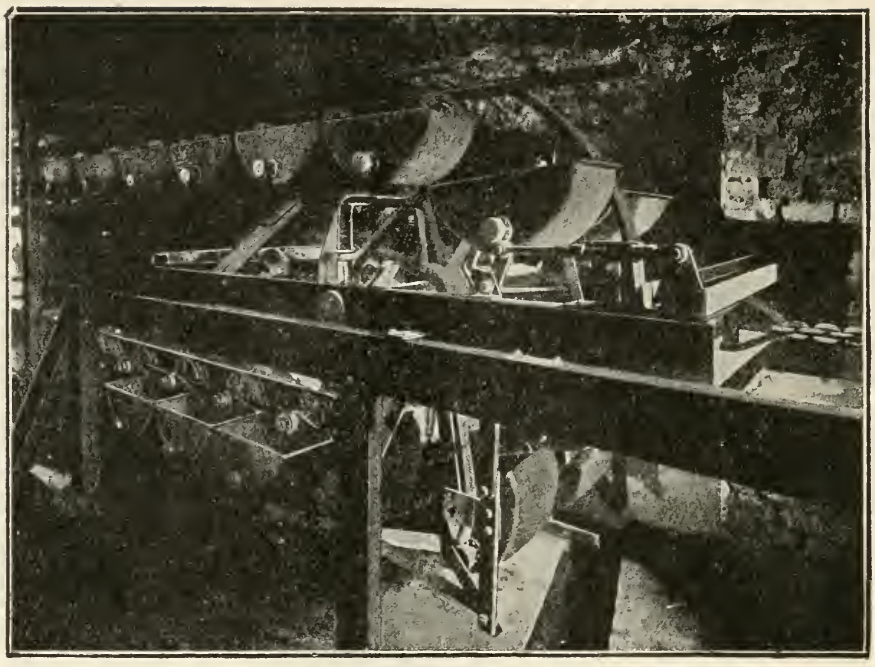
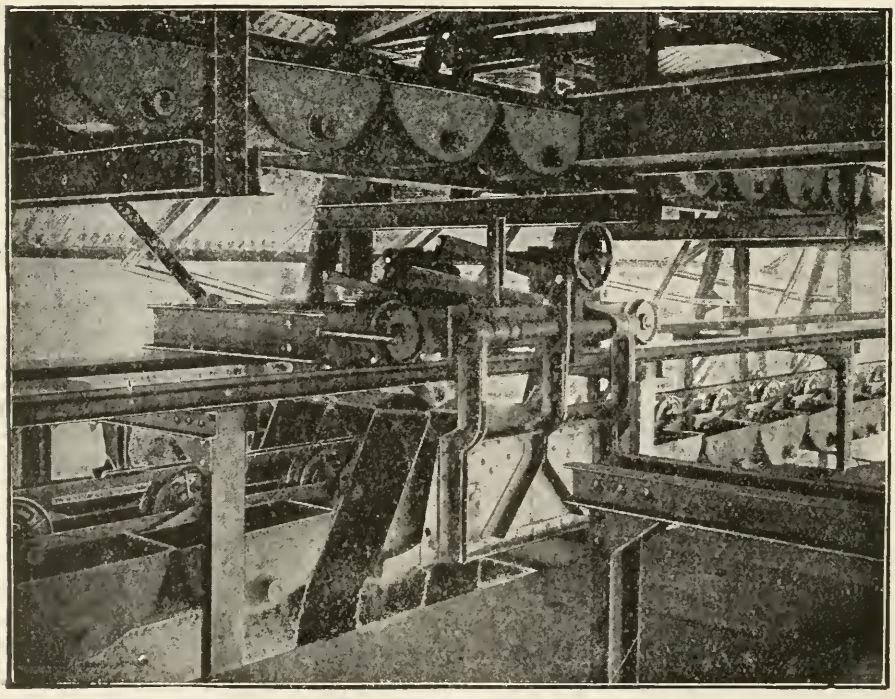


Fig. 54.—Section of Elevating Cups (Ad. Bleichert and Co.).

rigid robust aerial railways suitably sustained, but the principal obstacle to the extension of their system was that it barely attained a yield of 12 per cent, due to the want of proportion existing between the weight of the rolling car and that of the useful load to be conveyed. These weights were in fact in the ratio of 5 to 1. But if the first thing to be done was to reduce the weight of the car and the bin which form the truck as much as possible, taking into account the safety of the workmen, it was necessary also to create from the triple point of view of economy, simplicity and rapidity of transport, all the other parts of a complete installation. The plant and rolling stock for transport, such as the exigencies of modern factories demand, should include points and automatic safety apparatus, and above all the automatic travelling of the individual wagons independent of any handling as well as the greatest possible speed. The system devised by Ad. Bleichert and Co., owing to the ingenious arrangements of its rails, points, and curves, combines





FIGS. 55 and 56.—Electrical Conveyors (Ad. Bleichert and Co.).

this association of the greatest possible speed with the automatic working of the trucks, and certainly the solution of the problem should attract the attention of manufacturers, for it effects a remarkable saving in the working expenses of factories, particularly in chemical works. When the railway is on a level a single motor suffices, the rigid rail being generally fixed on a level. But in most cases it is necessary to span a difference of level between the point of departure and the point of arrival. It would be, moreover, very onerous to wish to employ a uniform slope throughout all the path of the railway, for it would involve a considerable expenditure of energy and a costly construction.

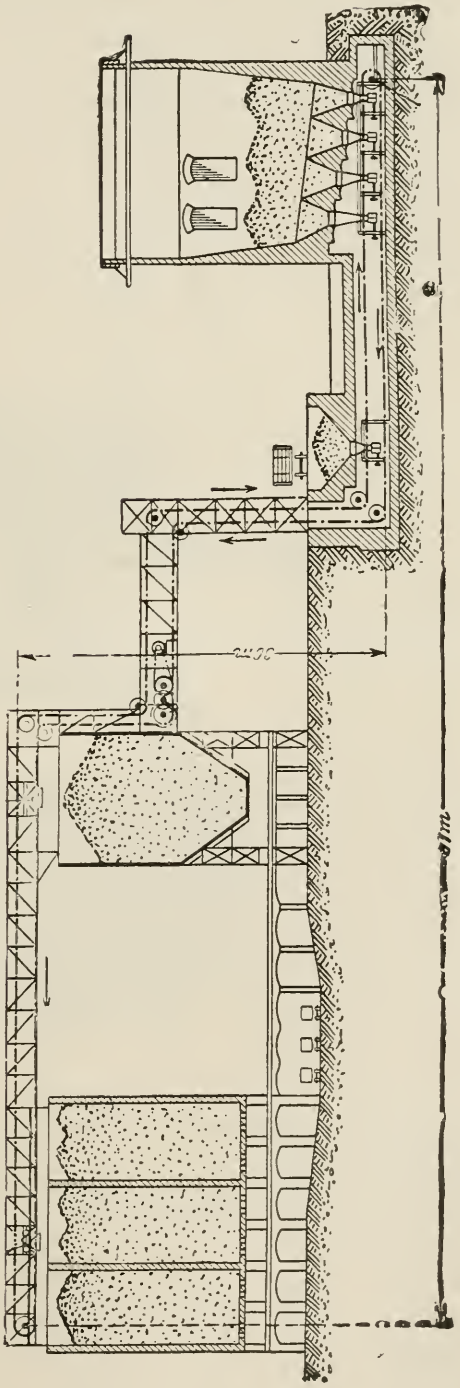


Fig. 57.—Cup-chain Elevator at work transhipping coal in a Chemical Factory (Ad. Bleichert and Co.).

The Bleichert system overcomes the difficulty in a practical manner by interposing in the network, suspended on bearings, trunk ways with desired incline, spanning the out of level whilst preserving enough free space to allow the wheels not to lose contact with the railway, and the bins to maintain their natural movement of oscillation. The advantage of this system consists especially in the fact that the limit need not be taken into account, for the sections are spanned by aid of organs absolutely independent of the driving of the cars. For this purpose the carrying track becomes a strong stair and rejoins in a few metres an upper part on bearings,

and on this stair the car is not driven by its own motor. A special system consisting of a motor and a chain or cable, running above the rail on the stair, pulls the car along in the following manner: A hook fixed in the car catches the chain which drives the fixed motor of the stair. The carrying system is drawn up to the moment when the hook quits it, which happens when the car reaches the elevated part or bearings. When the car catches on the stair the current from its own motor ceases, whilst it puts the cable in motion by means of another special motor which animates it with a uniform motion. At the moment when the car reaches the upper extremity of the inclined section, the inverse occurs. This

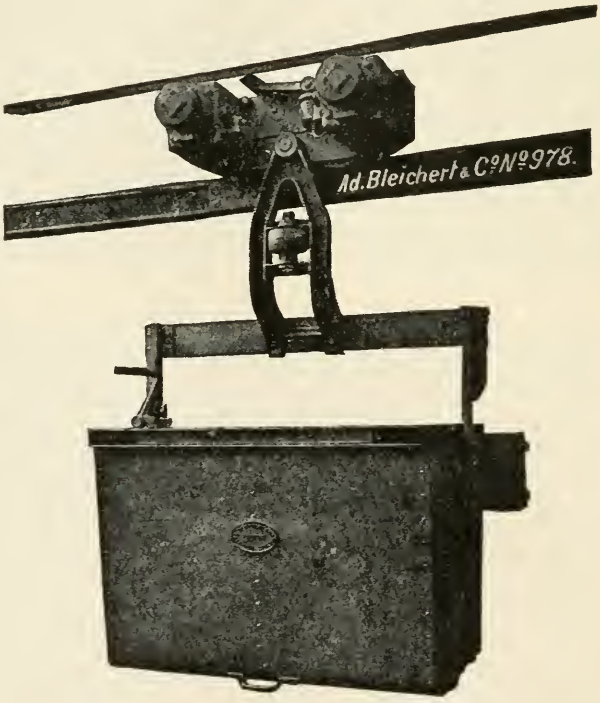


Fig. 58.—Electric Automotor Truck.

manner of traversing the stair is very advantageous; it permits a low-power motor to be used on the car. If the car motor had to ascend a considerable incline of itself, it would require to have a much greater force, hence a considerable weight increase of the section of the carrier, and consequently an increase of expense in the initial installation and working expenses (it would require in fact motors six to ten times more powerful per car). There are cases, however, where in consequence of considerations special to the problem to be solved, it is preferred instead of this mixed solution to solve the problem of removing material by means of independent arrangements enabling each to surmount the difficulties en-

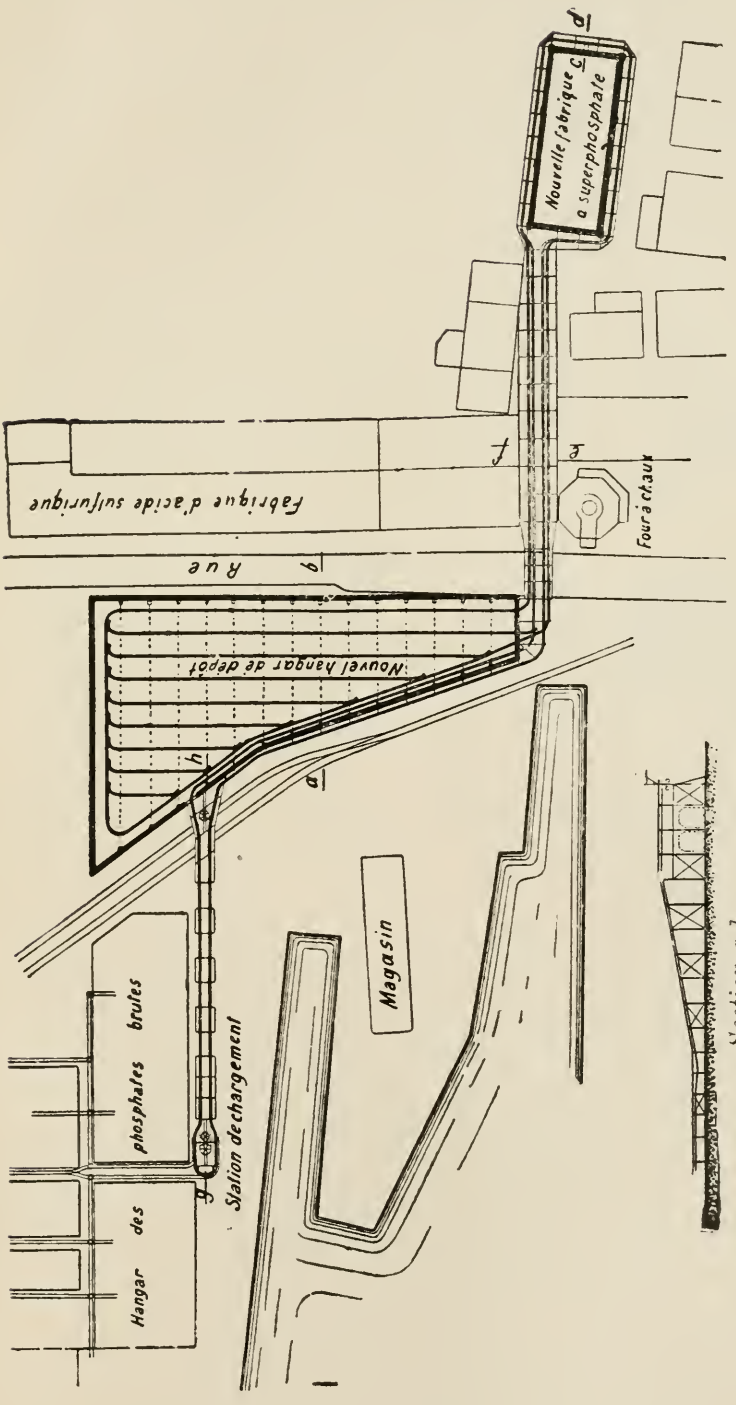


FIG. 59. — Electric Transhipment of Phosphate and Superphosphate in a Manure Factory.

Hangar des phosphates brutes = Raw phosphate shed. *Station de chargement* = Loading point. *Magasin* = Warehouse. *Nouvel hangar de dépôt* = New store shed. *Rue* = Street. *Fabrique d'acide sulfurique* = Sulphuric acid chambers. *Bâtiment du four à grevier* = (?) Pyrites kilns (burners). *Nouvelle fabrique à superphosphate* = New superphosphate factory. *Four à chaux* = Lime kiln.

countered. Automatic handling installations can in fact be seen consisting of a network of the system of cup-chain elevators combined with an electric network, or consisting of some one of these with the third system, that is to say the funicular rope system. For example, Fig. 59 shows a conveying installation in a superphosphate factory in which very considerable differences in level had to be spanned. It was a question especially of conveying the raw phosphate discharged from ships into a shed through the whole factory by an overhead railway to bring it into the superphosphate factory situated behind, and to lift the superphosphate there and deposit it in a shed from which it is charged into railway wagons. In these transfers all handling had to be avoided. The superphosphate shed is connected with the factory by a cable conveyor starting from the point *g*, and reaching about 8 metres (say 26 feet) in height, going round the factory and bringing its bins into a discharging hopper in which they are tip-tilted. The finished superphosphate is in its

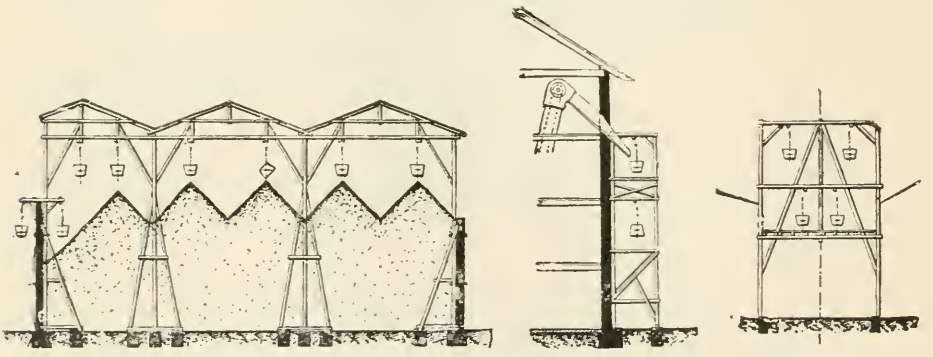


Fig. 60.—Section *a b* of Fig. 59. Section *c d*. of Fig. 59. Section *e f* of Fig. 59.

turn poured by means of an elevator into a hopper installed on the roof, from whence it is conveyed by means of an electric automatic superphosphate conveyor installed above the raw phosphate conveyor. The tilting of the bins in the hall of the depôt, their return and their stoppage at the point of loading, are carried out in an absolutely automatic manner. Fig. 64 shows the system of rolling and of tilting the electric superphosphate bins above their depôt; the sections of the figure (Fig. 60), *c d*, *a b*, *e f*, show the arrangement of the railways. There will be seen on the section *c d* the elevator described above, which serves to pour the superphosphate into the bins of the electric automatic system. This question of the elevation of material leads to the description of another method generally used to elevate material to levels capable of sometimes reaching 10 metres (33 feet) of vertical difference in level. The system of rope traction of cars, ordinary or electrical, on a stair to be spanned such as that shown in the section *g h* of Fig. 59, can only

be judiciously employed when the tonnage and the difference in level warrant it. For average tonnage and less, and for vertical differences in level up to about 6 to 7 metres, a special system of automotor car with crane is used such as shown in Fig. 61. It will be seen in that figure that between the bin and the car properly so called there is geared an electric crane with its commutators, magnetic brake and different arrangements to render the whole of the necessary manœuvres automatic once the current is applied to the whole of the car. By this system and by the aid of complementary arrangements of the line, the whole of the car can be arrested in any desired point of its course to pass the current automatically from the upper translating motor to the lower motor of descent, and of lifting, driving the crane at will; automatically to tilt the bin of its contents by the action of the electromagnet and its lifting crane, after which the empty bin coming to its highest position acts at the same time on a contact which again causes the current to pass from the elevating and descending crane to the propelling crane, and the whole of the car starts in motion again to return to the place where the bins are filled. The latter are filled by themselves at the hopper by a manœuvre, say exchanged against others filled between times in the course of the journey of the preceding ones. In general, these automotor cars consist of two cheeks of cast-steel firmly held together by cast-iron cross-pieces between which are lodged crucible cast-steel pulleys with deep grooves, the bosses of which turn freely on axes of phosphorous bronze acting as lubricating reservoirs. A wheel gearing with the steel pinion of the electric motor is fitted on the outside of one of these pulleys, and on the boss of the other a brake pulley is mounted, the band of which stretched on a powerful spring, on the type of a coach-spring, is automatically liberated when at work by an electromagnet. There are a very large number of these types of electrical cars, so as to respond to the different problems occurring in industry. For example, Fig. 62 shows a special system of car for spanning very sharp curves. There will also be seen from the figure the difficulties which had to be surmounted in a factory the free space of which at this point is restricted, as shown in

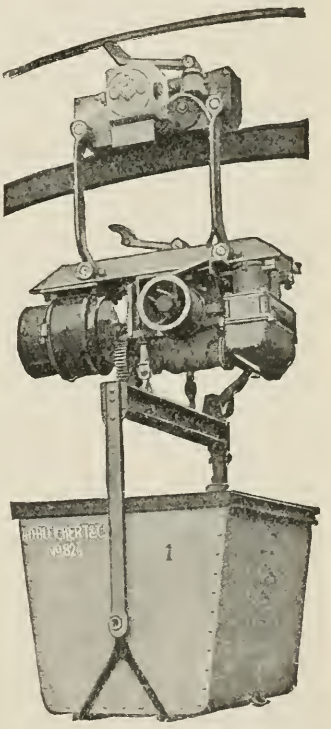


Fig. 61.—Special Automotor Electric Car with Crane.

the engraving. It also shows the use of bins with bilateral discharge by the unlatching of the system of closing of their side doors. Fig. 63 shows a bin of this system hooked to a special car with a specially arranged crane, and is used in the siloing of various

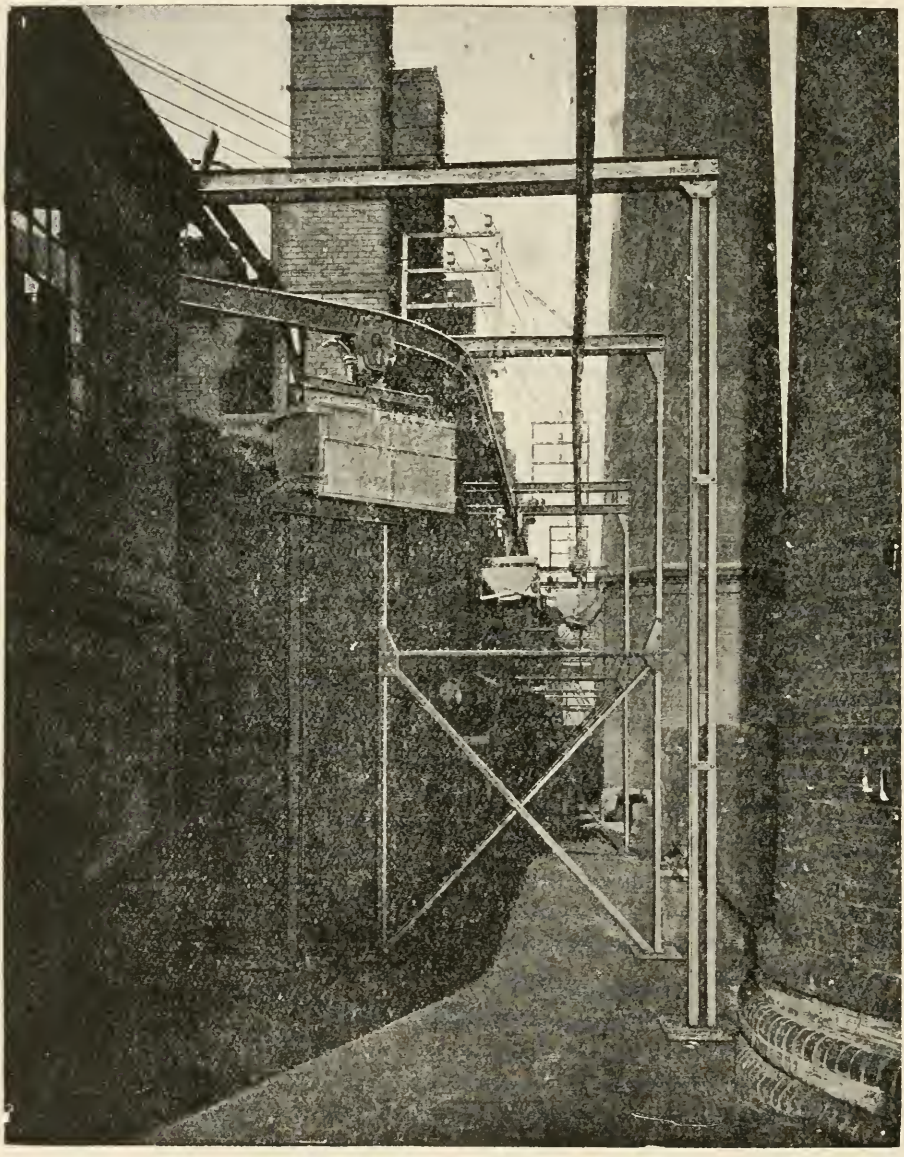


Fig. 62.—View of Special Electric Car Conveying System turning rapid Curves.

materials before being fed into the different hoppers. It will be seen that the bin shown in the engraving is fitted with a four-wheeled truck which enables it to run on Decauville rails in the space through which it proceeds to the filling of the bins. The most

important points of this system of electric traction must be described. If the railway is straight the speed may reach 2 metres (6 ft. 6 in.) a second. But this is not generally the case. A system often contains very sharp curves, in which the car and the suspended bin

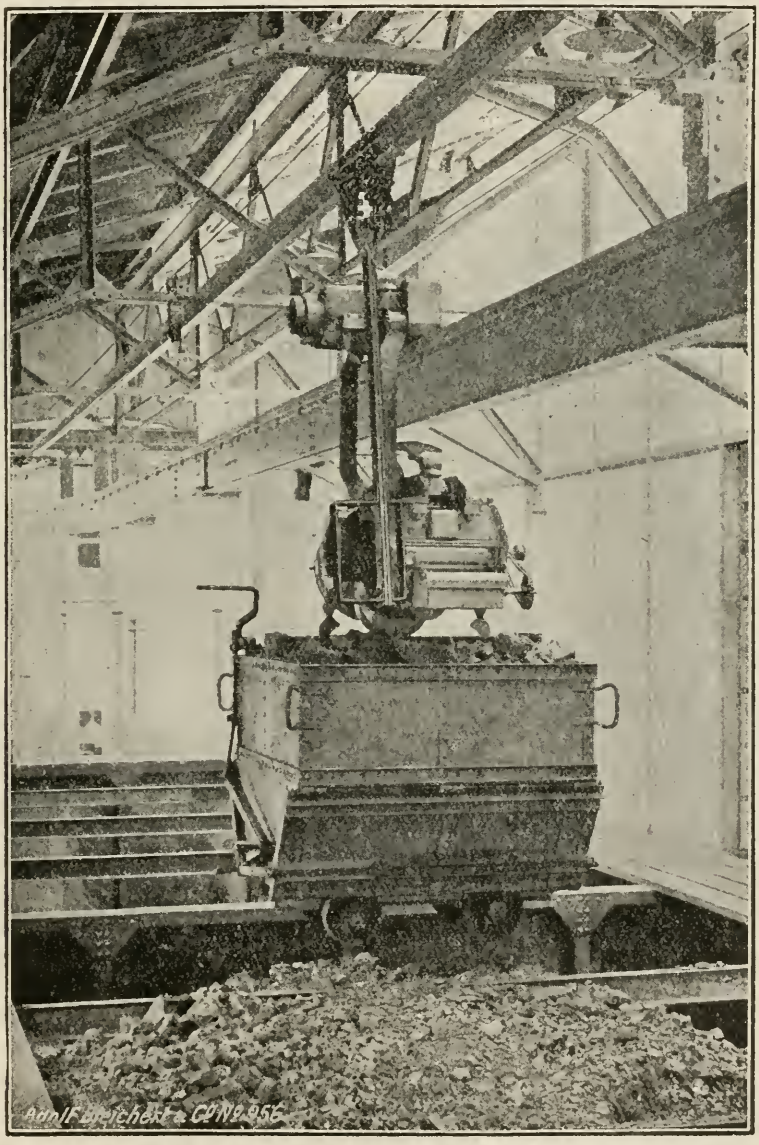


Fig. 63.—Electric Conveying Car at Silo.

ought to have a much lower speed than that given above. It will be seen that the centre of the system in motion being much lower than the railway on which it rolls, centrifugal force corresponding to the speed of 2 metres per second would cause the system to deviate appreciably from the vertical, which might cause mishaps.

To obviate this, in the Bleichert system resistances are fitted on the conductor at the passage of curves, so as to diminish the speed only in the curved part of the course; in the straight lines the speed is a maximum. Another peculiarity consists in the arrangement of the points; so long as the apex of the points is not well closed a commutator electrically isolates on the opening of the latter a certain length of conductor up to the points itself. The car then becomes stationary in front of the points if these are badly shifted, which avoids accidents. The length of this insulated trunk is such that the truck cannot reach the points in virtue of the acquired speed. When it is not a case of heavy freights, the most practical system is that in which the trucks accomplish a double journey on the same line; but in the case of important installations the railway is arranged in a circuit, so that the trucks can circulate in the same direction and follow each other continuously. So as to stop or start the trucks at any desired point, the naked conductor which transmits the energy to the trucks is divided into sections, insulated the one from the other, and as need be such and such sections are brought into circuit or out of circuit by simple commutators working automatically which can be placed at any necessary spot.

The division of the line into separate sections has the advantage of forming a block system, which prevents any collision automatically, and any shock between the trucks at the points or the crossings. Each truck reaching a section interrupts automatically by means of a commutator the current from the section it has just quitted, so that the wagon following, arriving on this section which is thus out of circuit, stops of its own accord. As soon as the first of the trucks just described arrives at the end of the section which we have seen it enter, it automatically turns a commutator, which re-establishes the current on the section on which the following wagon is standing, which can in this way continue its journey, repeating the preceding operations in the same cycle for the truck following. In that way no truck can reach crossings and points until the wagon which precedes is at a sufficient distance, and before it can pass them in its turn.

This arrangement, indispensable to any suspended electric railway on which a regular and safe service is required, produces at certain points—for example, where the trucks are filled—the following effects. The truck reaches the spot where it is filled, stops automatically, the current on the section on which it is placed having been cut by the truck ahead. The workman, the only one generally required for operating these installations, opens the valve which shuts the hopper, thus allowing the matter to run into the bin, and after having received its charge, brings the section into circuit. If, owing to fortuitous circumstances, the loading of the truck takes rather long, a larger number of wagons would arrive,

but it would be impossible for them to advance owing to the blocking of the line, and they would be forced to arrange themselves at regular intervals along the line. As soon as the charged truck starts, the following one advances automatically and stops at the hopper to receive its charge. The other trucks follow the lead and advance one after the other until their turn comes to take their place at the hopper, and the same routine goes on continuously.

As already mentioned, all supervision during the journey is absolutely superfluous, the trucks are unloaded automatically, for

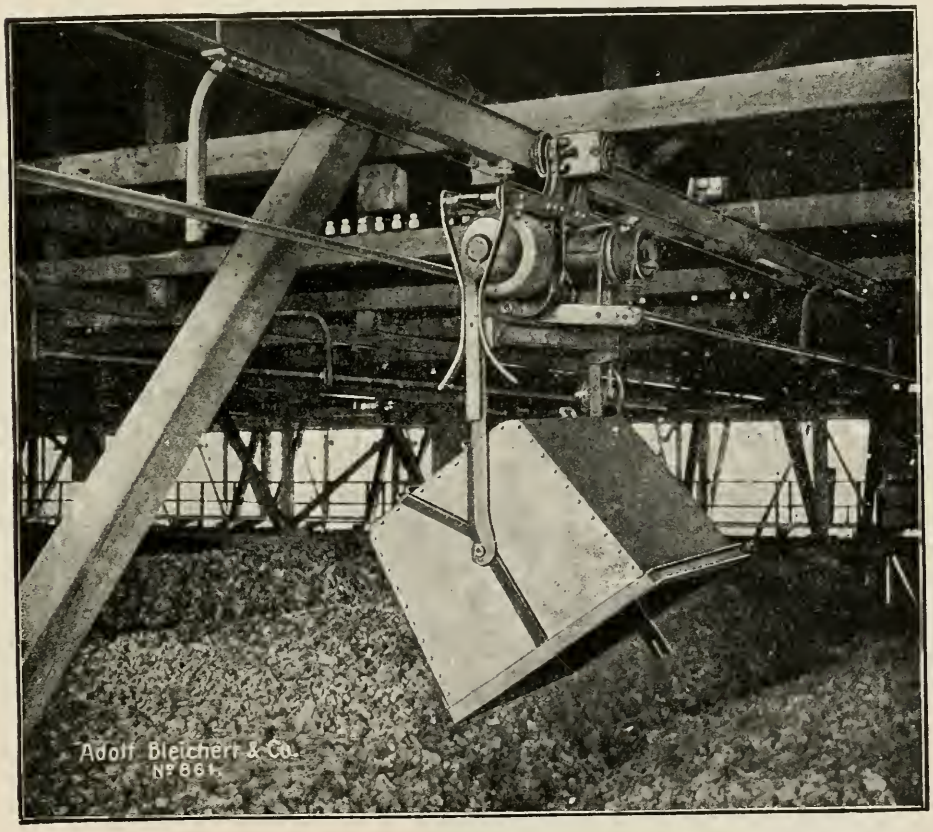


Fig. 64.—Electric Conveying Car tilting Contents into Silo.

the bolts which hinder the bin from tilting or which keep the sides of the bin closed, unlatch themselves during the working by means of a bolt. Owing to these arrangements it is possible to obtain great traffic on the whole line. These aerial railways on the electric automatic system may be supported outside the building on wood or metal brackets, leaving below them the necessary freedom for working in the factory and assuming, consequently, shapes appropriate thereto. At other times, as a measure of simplification or economy, these rails are hooked on to wall brackets or even to

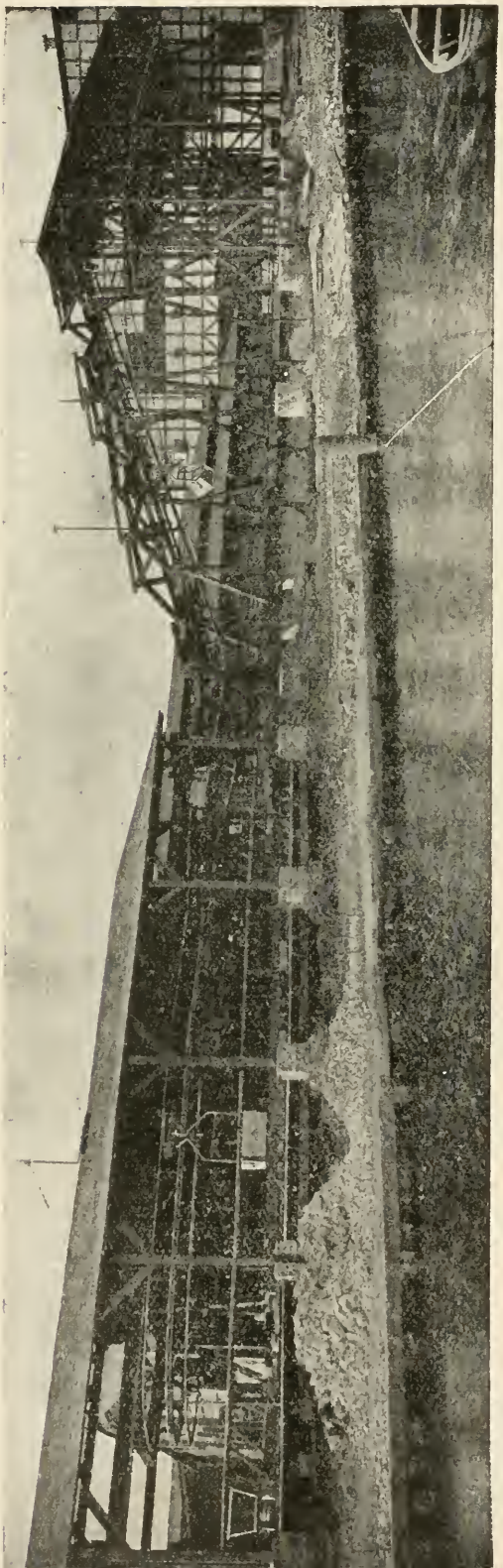


Fig. 65.—General Arrangement of Electrical Conveying Machinery in Pommersdorf Chemical Factory.

existing beams. Fig. 64 shows the automatic filling of silos by an electric railway suspended from old wooden beams, whilst Fig. 63 shows that the automatic electrical railway has been suspended from new metallic structures. The system of bin and car of Fig. 64 is a stout thick-set system in a vertical direction, taking into account that the old wooden beams of factories are at this point surbased, that they only allow of a small heap, and that thus all economy in the vertical height of the plant installed is particularly appreciated. On the other hand, in a new building like that of Fig. 63, the necessary vertical height can be calculated at leisure, profiting in the designing of the plant by the advantages of a sufficient height to instal an appropriate system of transport. This system, so remarkable and so simple in itself, insures the conveyance with a minimum of handling of big tonnages in as automatic a manner as possible.

The *Compagnie St. Gobain*, Chauny et Cirey, has just

erected at its Chantenay chemical works near Nantes an important installation of this nature. The photographs (Figs. 65-66) show as a whole similar installations in chemical factories and superphosphate factories. The first is the Pommersdorf chemical factory and the second the Emmerich chemical manure factory. These automatic conveying installations in factories where quantities of material are treated are of capital importance for go-ahead manufacturers desirous of lowering their wages bill and to place themselves as far as possible beyond the risk of strikes. It would lead us too far to develop all the applications which can be made of

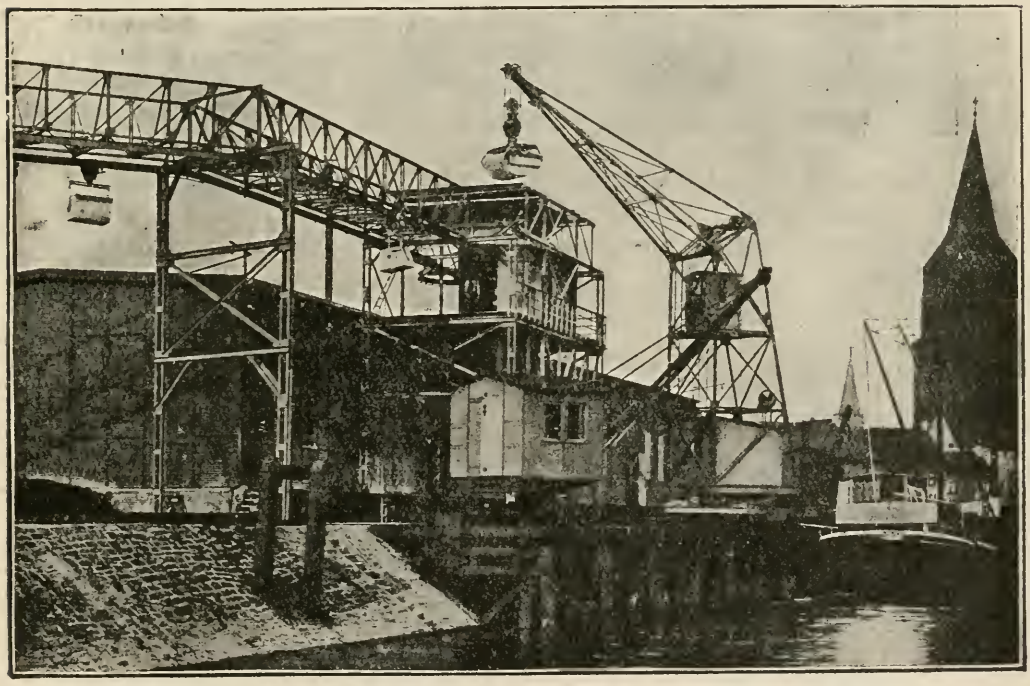


Fig. 66.—General Arrangement of Electrical Conveying Machinery in Emmerich Chemical Manure Factory.

this system, the more so as each new problem leads to a new solution. It is to be hoped that enough has been said for readers to have at their finger-ends all the advantages of these new systems which not only are already spread throughout France, but have more especially a considerable development abroad. We cannot terminate this slight review of these automatic conveyors without bringing to mind that the question of the automatic conveyance of raw materials from the ships or wagons in which they arrive is likewise an important question, especially for large factories. Fig. 67 shows the view of an automatic conveyor installed by the *Compagnie St. Gobain* at its Boucau chemical factory. Fig. 68 shows

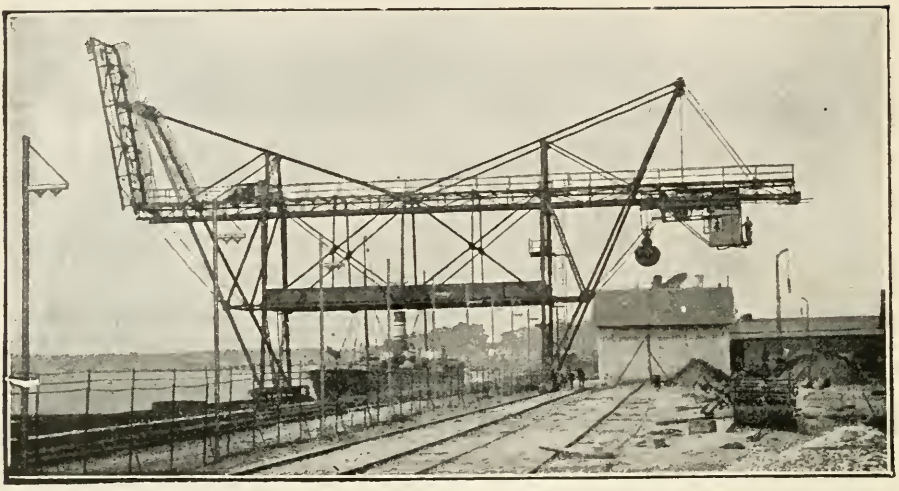


Fig. 67.—Electrical Transhipment Plant, St. Gobain's Chemical Factory, Boucau.

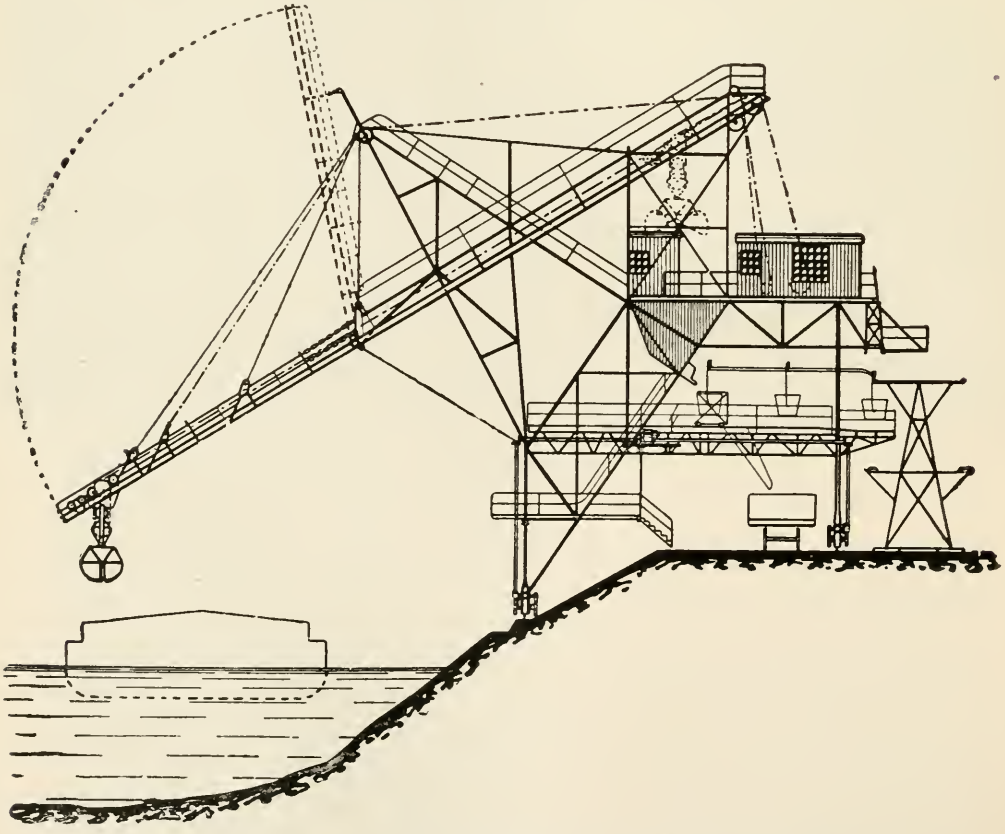


Fig. 68.—Electrical Transhipment Plant in a German Factory.

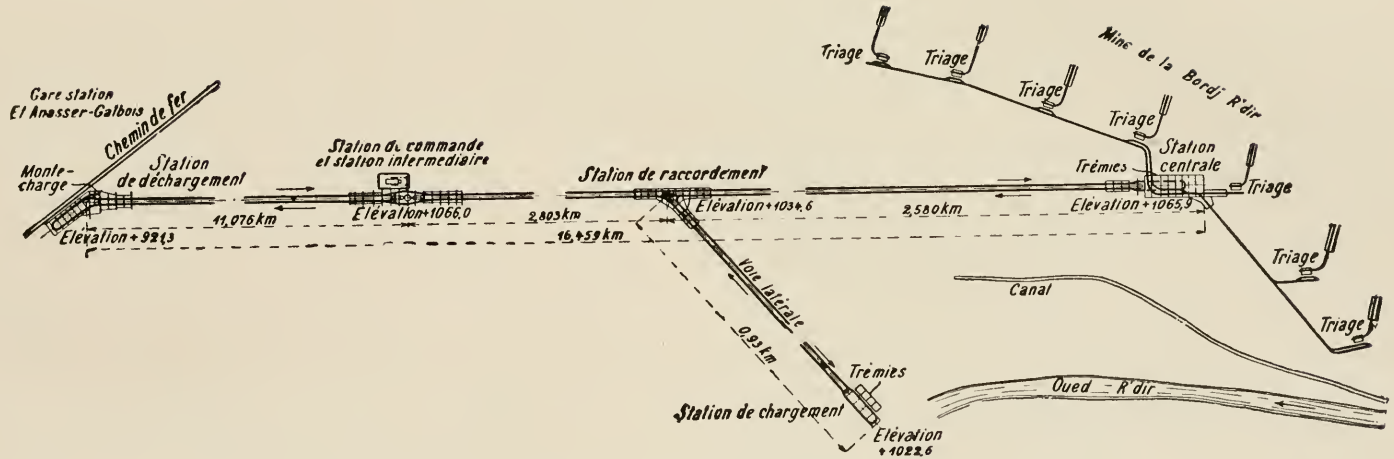


Fig. 69.—Cable Transhipment System of Algerian Phosphate Factory.

Gare station = Railway station.
Monte-charge = Elevator.
Station de commande et station intermediaire = Power station and intermediate station.
Station de raccordement = Marshalling station.
Mine de la Bordj R'dir = Bordj R'Dir phosphate mine.
Voie latérale = Branch line.
Oued R'dir = River of that name.
Chemin de fer = Railway.
Station de déchargement = Unloading station.
Trémies = Sieves.
Triage = Assortment.
Station de chargement = Loading point.

a conveyor of this nature installed for a German factory of chemical products by Ad. Bleichert & Co. Sometimes, as will be seen in Fig. 67, the cargo discharged from ships is simply disgorged by tilting-bins or slings into fixed or rolling hoppers or into rolling stock, or sometimes, on the other hand, these automatic transhipping installations are continued by automatic conveyors like those described above. The attention of those working phosphate deposits is drawn to the rope system adopted by the *Cie Centrale des Phosphates à Paris* for working its deposits of Bordj R'Dir.

There will be seen in Fig. 69 a considerable development of these rope railways which collect the phosphate into the great warehousing hoppers at the railway station of El Anasser Galbois, Algeria. Local considerations, the price of labour, the greater or less tonnage to be discharged and handled, the regular or intermittent manner in which these transhipments or shiftings occur, can alone afford, in each case, the necessary data to solve the problem in the most satisfactory manner in the interests of the manufacturer. The best course for manufacturers who occupy themselves with these questions more and more is to submit the problem to the study of specialists trained by constant practice.

INDEX.

A.

Abbeville, Somme, phosphates of, 14, 26.
Abrolhos guano, 39, 49, 58-9.
Acid, acetic, 13, 210.
— amount to use in dissolving various phosphates, 80.
— carbonic, 3, 11.
— citric, 13, 208, 210, 215.
— humic, 140.
— hydrochloric, 11, 74.
— hydrofluoric, 78, 110, 153, 154.
— hydrofluosilicic, 70, 71, 78, 154.
— metaphosphoric, 10.
— nitric, 11, 218, 224.
— — electrical production of, 271-7.
— orthophosphoric, 10.
— oxalic, 210.
— phosphoric, 1-13.
— — citrate, soluble, 138-40.
— — manufacture, 151-4.
— phosphorous, 9.
— pyrophosphoric, 8-9.
— silicic, 4, 154, 209-11, 213, 216.
— sulphuric, 11, 73-83.
— — treatment of bones by, 67.
— — — of mineral phosphates by, 67-72.
— — — quantity to use for various phosphates, 80-3.
— — — theory of same, 73-8.
— tartaric, 13, 210.
Adulteration, 22.
Aerial conveyors, 70, 316-31.
African phosphates, 58-9.
Ain-Beida phospates, 37.
Alabama River pebble phosphates, 34.
Albin, upper, 22.
Albumen, 10.
Alcantara phosphates, 29.
Alder, potash in ash of, 295.
Algerian phosphates, 36-8, 58-9, 71, 80, 82, 83, 132, 136.
Algerian phosphate warehousing plans, 331.
Algoa Bay guano, 49, 58-9, 286.
Allegri's automatic removal of superphosphate, 116.
Alta Vela phosphate, 39, 54-5.
Alumina, 78, 80.
Aluminic phosphates, 13, 80, 161-2.
— silicates, 80.
Amberg osteolite, 50-1.
America, North, apatite and phosphates, 29-31, 52-3.
— South, bone ash, 190-1.
— — nitrate of soda, 218.
— — guano, 277-86.
Ammonia blast furnace, 224, 226-8.
— from bones, 225-6.
— — coal, 228.
— — coke ovens, 226.
— — gas liquor, 225, 228-30.
— — — producers, 228-9.
— — — waste, 255.
— — peat, 244-9.
— — spent wash, 268-7.
— — urine, 243.
— in soot, 224.
Ammoniated superphosphate, 143.
Ammonium and magnesium phosphates, 12.
— and sodium phosphates, 11-12.
— chloride, 11, 224, 229, 280.
— citrate, 138-9.
— cyanide, 233.
— oxalate, 280.
— phosphate, 11-12.
— sulphocyanide, 251.
— urate, 280.
Angamos guano, 56-7.
Angaur, Isle of, 39, 48.
Anglo-Continental Guano Co., 197, 284, 285.
Animal charcoal, 191-2.
— debris, origin of phosphates, 4.
— waste, conversion of into manure, 253.
Apatite, 4 (pseudo do., 4), 11.
— Canadian, 29, 30, 52-3, 69, 81, 83.
— Norwegian, 27, 50-1, 69.
— Spanish, Estremadura, 28, 50-1.

Arabian phosphates, 38, 58-9.
Ardeche phosphates, 23.
Ardennes phosphates, 19-20, 50-1.
Ariège phosphates, 23.
Arkansas phosphates, 36.
Aruba phosphates, 39, 54-5, 83.
Ash of plants, potash in, 295.
Ashmore Island guano, 49.
Aube phosphates, 18.
Aubervilliers dried blood and meat meal factory, 256-62.
Australian phospho-guanos, 56-7.
Austria-Hungarian phosphates, 27, 50-1.
Auxois phosphates, 20-1.
Avalo Isle guano, 54-5.
Aves Isle phosphates, 39.

B.

Badajoz phosphates, 29.
Baker Isle guano, 39, 42-3, 46, 56-7, 68.
Ball mills (phosphate grinding), 70, 87, 96.
Barley straw, potash in, 295.
Barlow phosphates, 39, 42-3, 52-3.
Basalt, phosphorus in, 2.
Basic slag, 197-217.
Bat guano, 49, 58-9, 287-8.
Beauval phosphate, 16, 23.
Bedford coprolites, 52-3.
Beech, potash in, 295.
Beetles as manure, 294.
Belgian phosphates, 23-4, 50-1.
Bellegarde-sur-Rhône phosphates, 50-1.
Benzine, fat-extraction of bones, 182-4.
Bergkieserite, 39.
Bessarabia phosphates, 27.
Bicalcic phosphate, 138, 209.
Birds' excrement, 278.
Birds' Island guano, 49, 58-9.
Birkeland's nitrate of lime process, 272.
Black bone, 191-2.
Bleaching of bone fat, 184, 185.
Blood, dried, 256-62.
— drying of, 255, 259, 267, 294.
— in manure mixing, 190.
— phosphates, etc., in, 6.
Blue River phosphates, 32.
Bohemian apatite, 50-1.
Boiling meat for meat meal, 261.
Boncourt phosphates, 79.
Bone ash, 83, 177-8.
— bed, 26.
— black, 176-7.
— composition, 173.
— crushing, 177, 179.
— degelatinized, 181.
— dusts, 185, 186.
Bone earth. See Bone ash.
— fat, 179-185.
— meal. See Bone dust.
— mills, 177-9.
— picking, 176-7.
— steamed, 83.
Bones, bullocks', 176.
— buried, 176.
— butchers', 174.
— cattle, 176.
— classification, 176.
— grinding, 177-9.
— horse, 176.
— kitchen, 176.
— sheep, 176.
— storing, 175.
— vitriolized, 187-9.
Bonnes phosphates, 23.
Boulogne phosphates, 19, 20, 50-1.
Brachiopods, 3, 39.
Brain, phosphates in, 6.
Bromine from Stassfurt salts, 305.
Brown Island guano, 39, 44, 49, 58, 59.
Buenos Aires phosphate, 54-5.
Bukovina phosphates, 27.
Bullocks' heads, 176.
Burgundy lias, phosphates of, 20.

C.

Caceres phosphates, 50-1.
Cakes, filter press, 103.
Calais phosphates, 16-18.
Calcium aluminate, 206.
— carbonate, 53-9.
— chloride, 74, 306.
— fluoride, 11, 77, 194-5, 239.
— iodide, 77.
— phosphate, 4, 50-9, 73-5.
— silicate, 78, 200, 208, 308, 312.
— sulphate. See Gypsum.
— tetraphosphate. See Basic slag.
Caliche, 219.
Cambrian, Welsh phosphates of, 26.
Cambridge coprolites, 25, 52-3.
Canadian apatite, 52-3, 68-9, 81.
Cannes phosphates, 23.
Carbon disulphide, 3, 182.
Carbon in bone black, 192.
Carbonic acid, its function in manure manufacturing process, 76.
Carinthia phosphates, 50-1.
Carnallite, 297-309, 311, 313.
Carolina phosphates, 30-1, 52-3, 76-8, 80, 82-3.
Carr's disintegrator, 68, 118-9, 137, 144.
Cayman's Isle, 3, 39.
Charleston phosphates, 52-3.

Cheese, 294.
Cher phosphates, 22.
Chesterfield Isle guano, 39.
Chili guano, 56-7, 218.
Chinchas Isles guano, 56-7.
Chloroform, amount of fat ceded to, by various grades of bones, 186.
Christmas Isle guano, 41, 58-9.
Ciply phosphates, 23-4, 50-1, 83.
Clipperton guano, 39, 47, 49, 54-5, 83, 226-8.
Coke ovens, 226-8.
Colombine, 294.
Conveyors, 70.
Coprolites, 25-7.
Corcovado guano, 56-7.
Cracow bat guano, 50-1.
Crusher separator, 92-6.
Cup-chain elevator, 101.
Curaçao phosphates, 54-5.
Cyanimide, 272-7.

D.

Damaraland guano, 49, 58-9.
Damp superphosphate, 74.
Degelatinized bone dust, 186.
Delme osteolite, 50-1.
Den, manure mixing, 105-7.
Devonian formation, phosphates of, 29, 30.
Dicalcic phosphates, 11.
Dicyanamide, 274.
Dill phosphorite, 50-1.
Dimetallic orthophosphate, 10.
Discenides, 3.
Disintegrator, 100.
Dissolved bones, 187-9.
— leather, etc., 190.
— Peruvian guano, 284-6.
Distillery spent wash, ammonia, 268-72.
Dneister phosphate basin, 27.
Dolomite in super manufacture, 107.
Double superphosphate manufacture, 154-9.
Dried blood, 190, 255-62.
Drôme and Isère phosphates, 23.
Drying blood, 255-9.
— in vacuo, 257.
— raw phosphates, 60.
— superphosphates, 81, 121 *et seq.*
Dry mixing of manures, 142.

E.

Eagle, dung of, 278.
Eboli bat guano, 288.
Edge-runner for grinding raw phosphates, 85.
Effront's fermentation ammonia, 270-2.
Egyptian phosphates, 38, 58-9.
Electrical conveyors, 316-33.
Electric furnace, manufacture of phosphorus in, 167-72.
Elevating phosphoric acid, 154.
— raw phosphates, 101.
— sulphuric acid, 105.
Enderbury Island guano, 39, 49, 56-7.
English phosphates, 25-7.
Estremadura apatite, 5, 29, 50-1.
Experiments on hay, 140-1.
— on oats, 129.

F.

Falkland Islands guano, 54-5.
Fanage of raw phosphates, 62.
Fanning Island guano, 39, 44, 49-50, 56-7.
Fans of superphosphate dens, 110.
Fat, bone-extracting and bleaching, 179-85.
Feldmann's steam still for ammonia liquor, 241.
Felixtowe coprolites, 26.
Felspar, electrolytic extraction of potash from, 314.
Ferns, potash in ash of, 295.
Ferric chloride, 12.
— oxide, 12, 79.
— phosphate, 12.
Ferrous oxide, 13, 139, 211.
— phosphate, 211, 213.
— sulphate, 78-9.
— sulphide, 78.
Fertilizing value of basic slag, 196-8.
— — of bones, 175.
— — of cyanamide and nitrate of lime, 274-7.
— — of meta and pyrophosphates, 129.
— — of phosphate of potash, 164.
— — of potash salts, 310-3.
Filter press, 103-4, 164.
— — plates, pitch pine, 152.
Fish guano, 267, 275, 290.
— waste, 294.
Flint Isle guano, 39.
Florida phosphate, 30-5, 52-3, 69-71, 82-3.
Fluorine, 77, 154, 175.
Free phosphoric acid, 74.
Frigatte Shoal guano, 49.
Fuel used in drying superphosphate, 128.
Fumes from mixer, condensing, 70, 107, 109.
— — meat boiling, condensing, 262.

G.

Gafsa phosphates, 37, 58-9, 71, 82-3, 130.
Galapagos guano, 40.
Galician bat guano, 49.
— phosphates, 27.
— salt and potash deposits, 297.
Gard and Ardeche phosphates, 23.
Gas liquor, 225-8, 230.
— Mond's, 228-9.
— purification waste, 255.
— Siemens', 228-9.
Gault clay, phosphates of, 17, 21.
Gelatine, extraction of, from bones, 179, 181.
George Isle phospho guano, 54-5.
Glauconitic sand, 21.
Gneiss, 2.
Goodrich mineral phosphates, 52-3.
Granulet, 2.
Greaves, 294.
Green manuring, its rôle in the future, 289.
Grinding bones, 177-9.
— raw phosphate, 84-9.
Guanahani phospho guano, 52-3.
Guano, Abrolhos, 39, 49, 58-9.
— Algoa Bay, 49, 58-9, 286.
— Angamos Island, 56-7.
— Angaur Island, 48.
— Ashmore Island, 49.
— Avalo Island, 54-5.
— Aves Island, 39.
— Baker Island, 39, 46, 68.
— Ballestas, 56-7.
— bat, 49, 58-9, 287-8.
— Birds' Island, 49, 58-9.
— Brown Island, 39, 49, 58-9.
— Cayman's Island, 39.
— Chincha Isles, 56-7.
— Christmas Isles, 38-9, 41, 71.
— Clipperton, 39, 49, 83.
— Corcovado, 56-7.
— crab, 293.
— Damaraland, 49, 58-9.
— Eboli bat, 288.
— Enderbury Island, 49, 56-7.
— Falkland Islands, 54-5.
— Fanning Island, 49-50, 56-7.
— fish, 267, 275-94.
— Fray Bentos, 263.
— Galapagos, 49.
— Galician bat, 49.
— George Isle, 54-5.
— Guanahani phospho, 52-3.
— Guanape, 56-7.
— Howland Islands, 49, 56-7.
Guano, Huanillos, 56-7.
— Huon Island, 58-9.
— Ichaboe, 49, 58-9, 286.
— Independencia Bay, 56-7.
— Jarvis Isle, 43.
— Jones Island, 49, 56-7.
— Kurian Murian, 49, 58-9.
— Lacépède, 39, 49, 58-9.
— Leysan Isle, 49.
— Lobos de Afuera, 56-7.
— Lobos de Tierra, 56-7.
— Los Aves Isles phospho, 54-5.
— Los Roques, 54-5.
— Macabi, 56-7.
— Makatea, 48.
— Malden Island, 49, 56-7, 83.
— Maracaibo (Monkey Island), 54-5.
— Mary, 49, 56-7.
— Mejillones, 45, 46, 49, 56-7, 68.
— Monk's Island, 49.
— Nauru, 48.
— Norwegian fish, 267, 275.
— Ocean Isle, 56-7.
— Pabellon de Pica, 56-7.
— Patagonian, 49, 54-5.
— Peruvian, 49, 56-7, 83, 277, 286.
— Porto Rico bat, 52-3.
— Punta de Lobos, 56-7.
— Raza, 54-5.
— Shark's Bay, 49, 56-7.
— Sombrero, 40, 54-5, 83.
— Starbuck, 49, 56-7.
— Timor Island, 49, 58-9.
— Vivorilla Island, 49.
Guelma phosphate, 37.
Gypsum, 11, 73, 74, 75, 153, 157, 158.

H.

Hair, bullocks', 294.
Hallencourt phosphates, 14.
Hardvilliers phosphates, 14.
Hartz apatite, 50-1.
Hautes Marne phosphates, 20.
Havana phosphates, 52-3.
Helmstedt phosphorite, 50-1.
Hens' dung, 218.
Hoof and horn dust, 267, 294.
Horde phosphorite, 50-1.
Horn dissolving, 190, 263-5.
— liquor, 265.
Hornpiths, 176.
Howland Island guano, 49, 56-7.
Huanillos guano, 56-7.
Human skeleton, 6-7.
Humus, 140.
Huon Island guano, 58-9.
Hydrogen sulphide, 243.

I.

Ichaboe guano, 49, 58-9, 286.
Ichthyocol, 80.
Ichthyosaurus, 25.
Iodine in phosphates, 77.
— in nitrate, 220-1.
Ipswich coprolites, 52-3.
Iron acetates, 13.
— and alumina, phosphates of, 78-80, 133, 155.
— oxide, 2.
— phosphate, hydrated, 78-80.
— phosphate of, 12, 13, 139, 211.
— sulphate, 78-9.
— sulphide, 78.
Italian phosphates, 50-1.

J.

Jarvis Island guano, 39, 43-4, 49, 58-9.
Jaw-breaker mills for raw phosphate, 96-7.
Jones Island guano, 49, 56-7.

K.

Kainit, 299, 300, 309, 311.
Kieserit, 306, 309, 311.
Knackers' bones, 176.
Koerting's injector, 221.
Krageroe apatite, 50-51.
Krugite, 301.
Kuban potash (sunflower), 314-5.
Kurian Murian guano, 49, 58-9.
Kursk phosphorite, 52-3.

L.

Lacepedes guano, 39, 45, 49, 58-9.
Lahn phosphorite, 50-1, 136, 151.
Lair's, de, di-ammonia still, 238.
Lamming's mixture, 251.
Land phosphates, 34-5.
Langesund chlorapatite, 50-1.
Lavanthal phosphorite, 50-1.
Lawes and Gilbert's experiments, 312-3.
Lead-lined vessels, 153.
Leather, dissolving, 190-1, 265-7.
— grinding, 190.
— shavings, 294.
Leysan Isle guano, 49.
Lias phosphates, 20.
Liebig's theory, 151.
Liége phosphates, 23-4, 50-1, 83.
Ligulides, 3.
Lime, milk of, 195, 224, 233-4, 238, 241-3.
Lobos de Afuera guano, 56-7.
Lobos de Tierra guano, 56-7.
Logrosan phosphorite, 52-3.
Los Aves Isle phospho guano, 54-5.
Los Roques guano, 39, 54-5.
— — iron phosphates, 54-5.
Lot phosphates. See Quercy.
Lunge's ammonia still, 238.
Lutjens' superphosphate drier, 125-8, 136-7.
Lyme Regis phosphates, 25, 52-3.

M.

Macabi guano, 56-7.
Magnesia, 77, 211.
Magnesium and potassium, double sulphate of. See Kainit.
— carbonate, 107.
— chloride, 305, 308, 309.
— phosphate, 77.
— silicate, 312.
— sulphate, 107, 307.
— tetraphosphate, 211.
Maikopp potash factories, 314.
Maize, potash in ash of, 295.
Makatea guano, 39, 48.
Malden Island guano, 39, 49, 56-7, 83.
Malogne phosphates, 154.
Maracaibo guano, 54-5.
Mary Island guano, 49, 56-7.
Meadows, manure for, 141, 148.
Measuring tank, acid, 107.
Meat meal, 186-7, 259, 260-1, 294.
Mejillones guano, 45, 46, 49, 56-7, 68.
Metaphosphate of lime, 129, 154.
Meuse phosphates, 18-19.
Mexican phosphates, 68.
Microbicide, phosphatic peat as, 165.
Mills for grinding bones, 177-9.
— — — raw phosphates, 84.
Minerva Isle guano, 39.
Mixer, superphosphate, 105, 110.
Mixing trials, 82.
Mona Isle guano, 39, 49, 54-5.
Mond gas, ammonia plant, 229-230.
Monk's Isle guano, 41, 49.
Monocalcic phosphates, 10, 11, 165.
Monometallic orthophosphate, 10.
Muriate of potash, 301-15.

N.

Naphthenes, 80.
Nauru guano, 39, 48.
Navassa phosphates, 39, 40, 49, 54-5, 68.
Nettles, potash in, 295.
New York apatite, 52-3.
Nitrate of ammonia 275.

Nitrate of lime, 11, 271-7.
— of manganese, 223.
— of potash, 218, 222, 294.
— of silver, 218.
— of soda, 140, 218, 294.
— — — boiling-point of solutions, 221.
Nitric acid, 218.
— nitrogen, 275.
Nitrogen, ammoniacal, 275.
— nitric, 275.
Nitrophosphate, 148.
Nitrous sulphuric acid as solvent for leather, etc., 191.
Norwegian apatite, 27, 69.
— fish guano, 292.

O.

Oak filter press frames, 152.
— potash in ash of, 295.
Oats, experiments on, 129.
Ocean Isle phosphates, 56-7.
Ontario apatite, 52-3.
Organism, function of P_2O_5 in, 3.
Orthophosphoric acid, 8-10, 129-33.
Orville phosphates, 14, 15, 16.
Ossein, 195.
Osteolite, 50-1.
Ottawa apatite, 52-3.

P.

Pabellon de Pica guano, 56-7.
Palestine phosphorite, 58-9.
Pas de Calais phosphates, 15, 16-18.
Patagonia East Coast guano, 54-5.
Patagonian, 49, 54-5.
Peace River phosphates, 34-5, 52-3.
Pebble phosphates, 82-3, 136.
Peine coprolites, 50-1.
Permian saurians, 3.
Pernes phosphate basin, 14.
Phœnix Isle guano, 39, 49, 56-7.
Phosphates, acid required to dissolve, 80.
— drying and enrichment, 60-66.
— geological distribution, 49.
— raw, description and geographical distribution of deposits, 14, 59.
Phosphoric acid, 1-10.
— — manufacture, 151-4.
Phosphorus, 1-8.
— manufacture, 167-172.
Pigeon dung, 278.
Pine, potash in, 295.
Plum tree wood for phosphoric acid, 152.
Podolian phosphates, 52-3, 83.
Polk Co. phosphates, 34.
Pollen, phosphorus in, 6.
Polyhalite, 300.
Portugal apatite, 29.
Port Royal phosphate, 52-3.
Potash salts, 309, 311, 315.
— — Russian, from sunflower, 315.
Potassium and magnesium double sulphate, 307.
— — — — phosphate, 309.
— carbonate, 295.
— chloride, 215, 297, 315.
— nitrate, 218, 222, 294.
— silicate, 309.
— sulphate, 309-11.
— superphosphate, 146-9.
Precipitated phosphate manufacture, 83.
Puerto Rico bat guano, 52-3.
Pump for phosphoric acid, 154, 158-9.
— precipitated phosphate filter press, 195-6.
Punta de Lobos guano, 56-7.
Pyrenees phosphates, 23.

Q.

Quercy (Lot) phosphates, 22, 50-1.
Quick-speed bone crusher, 178.

R.

Rata phosphates, 39, 49, 54-5.
Raza Island guano, 54-5.
Redonda phosphate, 39, 41, 49, 54-5.
— — utilization of, 161-4.
Reduced phosphates, 151.
Reeds, potash in ash of, 295.
Remover, automatic, of superphosphates from den, 112-7.
Retrogradation (reduction) of phosphates, 151.
Rocks, primitive P_2O_5 in, 2.
Roller mill toothed for raw phosphates, 97.
— — double for raw phosphates, 96.
Russian black earth, *Tchermo Sem*, 5.
— phosphates, 28, 52-3.

S.

St. Martin's phosphates, 49, 54-5.
Sal ammoniac, 294.
Saldanha Bay guano, 58-9.
Salt, common, 306.
Sardinian bat guano, 49, 50-1.
Saurians, 3.

Schlaggenwald apatite, 50.
Schoenite, 309.
Sea-fowl excrement, 278.
Seed, phosphates in, 6.
Setif phosphates, 37.
Sfax phosphates, 58-9.
Shark's Bay guano, 49, 56-7.
Sidney Island guano, 39, 56-7.
Sieves, 87-91, 102.
Sifting machine, 102.
Silicates, calcic, 312.
Silicic fluoride, 110.
Silkworm litter, 294.
Silurian fish, 3.
Skin debris, 175.
Slow-speed bone crusher, 177.
Sodium and ammonium phosphates, 11, 12.
— phosphates, 11, 12.
Soil migration of phosphoric acid in, 3-4.
— superphosphates become insoluble in the, 129.
Solubility of phosphates in soil, 140-1.
Sombrero phosphates, 39, 49, 54-5, 83.
Somme phosphates, 14-16, 50-1, 82-3, 154.
South Carolina phosphates, 30.
Spanish phosphates, 5, 50-3.
Stamping mill, 99.
Starbuck Island guano, 39, 49, 56-7.
Starkenbach coprolites, 50-1.
Steam stills for ammoniacal liquor, 240.
Stercorite, 12.
Struvite, 12.
Suffolk crag, 26.
— coprolites, 26.
Sulphophosphates, 160.
Superheated superphosphate, 129.
Superphosphate, bone, 187-9.
— of ammonia, 143.
— — and potash, 146.
— drying, 81.
— historical review, 67-72.
— manufacture, 84-110.
— mixing, 105-10.
Superphosphate, shifting (mechanical), 116.
— sifting, 68, 137.
— storing and retrogradation, 111.
Swan Island guano, 49.
Syenite, phosphorus in, 2.
Sylvinite, 298, 309, 311, 313.

T.

Tallahasee phosphates, 52-3.
Tebessa phosphates, 37, 58-9.
Teleosaurus, 25.
Tennessee phosphates, 52-3, 82, 83, 137.
Testigos phosphates, 49, 54-5.
— iron phosphates, 54-5.
Timor Island guano, 49, 58-9.
Toothed roller mill, 97.
Toqueville phosphates, 58-9.
Tricalcic phosphates, 50-59.
Truxillo phosphates, 52-3.
Tunis phosphates, 49, 58-9.

V.

Vasseux fermentation process for recovery of ammonia from spent wash, 269-70.
Vaucluse phosphorite, 50-1.
Vetches, potash in ash of, 295.
Vine, potash in ash of, 295.
Vitrolized bones, 187-9.
Vivorilla Island guano, 49, 52-3.

W.

Wagner's researches on basic slag, 197.
Wales phosphate, 52-3.
Wasserleben phosphorite, 50-1.
Waste products, conversion into manure, 255-267.
West Indian phosphates and phospho guanos, 49, 52-55.
Whale guano, 293.
Wheat straw, potash in ash of, 295.
Willow, potash in ash of, 295.
Wool, waste rags, etc., 194, 265.
Woronesch phosphate, 52-3.

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INDEX TO SUBJECTS.

	PAGE
Agricultural Chemistry	10
Air, Industrial Use of	12
Alum and its Sulphates	9
Ammonia	9
Aniline Colours	3
Animal Fats	6
Anti corrosive Paints	4
Architecture, Terms in	29
Architectural Pottery	15
Artificial Perfumes	7
Balsams	10
Bibliography	32
Bleaching	23
Bleaching Agents	23
Bone Products	8
Bookbinding	31
Brick-making	14, 15
Burnishing Brass	27
Carpet Yarn Printing	21
Casein	4
Celluloid	31
Cement	29
Ceramic Books	14, 15, 16
Charcoal	9
Chemical Essays	9
Chemical Works	26
Chemistry of Pottery	16
Chemistry of Dye-stuffs	22
Clay Analysis	16
Coal-dust Firing	26
Colour Matching	22
Colliery Recovery Work	25
Colour-mixing for Dyers	22
Colour Theory	22
Combing Machines	24
Compounding Oils	6
Condensing Apparatus	26
Cosmetics	8
Cotton Dyeing	22
Cotton Spinning	24
Cotton Waste	22
Damask Weaving	20
Dampness in Buildings	29
Decorators' Books	28
Decorative Textiles	20
Dental Metallurgy	25
Drugs	30
Drying Oils	5
Drying with Air	12
Dyeing Marble	30
Dyeing Woollen Fabrics	22
Dyers' Materials	22
Dye stuffs	23
Edible Fats	7
Edible Oils	7
Electric Wiring	27
Electricity in Collieries	25
Emery	32
Enamelling Metal	18
Enamels	18
Engraving	31
Essential Oils	7
Extracts, Wood	29
Evaporating Apparatus	26
External Plumbing	27
Fats	5, 6
Faults in Woollen Goods	21
Flax Spinning	24
Foods and Drugs	30
Fruit Preserving	30
Fungicides	28
Gas Firing	26
Glass-making Recipes	16
Glass Painting	16
Glue Making and Testing	8
Greases	5
Hat Manufacturing	20
Hemp Spinning	24
History of Staffs Potteries	16
Hops	28
Hot-water Supply	28
How to make a Woollen Mill Pay	21
India-rubber	13
Industrial Alcohol	10
Inks	3, 11
Insecticides	28
Iron-corrosion	4
Iron, Science of	26
Japanning	28
Jute Spinning	24
Lace-Making	20
Lacquering	27
Lake Pigments	2
Lead and its Compounds	11
Leather Industry	13
Leather-working Materials	14
Libraries	32
Lithography	31
Lubricants	5, 6
Manures	8, 10, 11
Meat Preserving	30
Mineral Pigments	3
Mineral Waxes	6
Mine Ventilation	25
Mine Haulage	25
Mining, Electricity	25
Needlework	20
Oil and Colour Recipes	3
Oil Boiling	5
Oil Merchants' Manual	6
Oils	5
Ozone, Industrial Use of	12
Paint Manufacture	2
Paint Materials	3
Paint-material Testing	4
Paint Mixing	28
Paper-Mill Chemistry	17
Paper-pulp Dyeing	17
Petroleum	6
Pigments, Chemistry of	2
Plumbers' Work	27
Pottery Clays	16
Pottery Decorating	15
Pottery Manufacture	14
Pottery Marks	16
Power-loom Weaving	19
Preserved Foods	30
Printers' Ready Reckoner	31
Printing Inks	3
Recipes for Oilmen, etc.	3
Resins	10
Risks of Occupations	12
Riveting China, etc.	15
Sanitary Plumbing	27
Scheele's Essays	9
Sealing Waxes	11
Silk Dyeing	22
Silk Throwing	18
Smoke Prevention	26
Soaps	7, 8
Spinning	21
Spirit Varnishes	5
Staining Marble, and Bone	30
Steam Drying	12
Sugar Refining	32
Steel Hardening	26
Sweetmeats	30
Tanning Extracts	29
Technical Schools, Hand-book to the	32
Terra-cotta	15
Testing Paint Materials	4
Testing Yarns	20
Textile Fabrics	18, 19
Textile Fibres	19, 24
Textile Materials	20
Timber	29
Varnishes	5
Vegetable Fats	6
Vegetable Preserving	30
Warp Sizing	21
Waste Utilisation	11
Water, Industrial Use	12
Water-proofing Fabrics	21
Waxes	6
Weaving Calculations	21
Weed Killer	28
White Lead and Zinc	4
Wood Distillation	29
Wood Waste Utilisation	29
Wood-Dyeing	30
Wool-Dyeing	22, 23
Writing Inks	11
X-Ray Work	13
Yarn Sizing	21
Yarn Testing	20
Zinc White Paints	4

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